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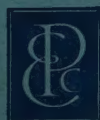
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M. Peligot finds uranium

M. Peligot has communicated to the Annales de Chimie et Physique (xvii, 363) a short note on the preparation of uranium. A mixture of 75 grammes of uranous chloride, 150 grammes of dry potassium chloride, and 50 grammes of sodium in fragments is introduced into a porcelain crucible, itself surrounded by a plumbago crucible. The reaction is effected in a wind furnace at the temperature of redness; but the heat must be increased for a short time at the close of the operation. In the black slag may be found, after cooling, globules of fused uranium.



The new method of producing uranium was announced in the first issue of *Nature* in 1869. Monsieur Peligot, who twenty-eight years before had first isolated the metal, discovered by Klaproth in 1789, was opening the door a little more widely to the possibility of an Atomic Age a century later. In recent years the priority attaching to the atomic energy programme has restricted their availability, but uranium compounds are now again available and figure among the several thousand fine chemicals of very high purity supplied by B.D.H. for science and industry. The B.D.H. catalogue contains more than 6,000 laboratory chemicals and reagents. Of these some hundreds in addition to 'AnalaR' and 'M.A.R.' chemicals, are labelled with specifications of purity.

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CHLOROMETHYLATION OF 8-HYDROXYQUINOLINE

by

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Several workers have reported that formaldehyde reacts with 8-hydroxyquinoline in the presence of alkali, sulphuric acid or hydrochloric acid, and that the products obtained were carbinols or diquinolylmethanes¹⁻⁶. A Swiss patent⁷ describes the preparation of a derivative of 8-hydroxyquinoline by saturating a mixture of formaldehyde and 8-hydroxyquinoline in hydrochloric acid solution, with hydrochloric acid gas. The conditions employed in this preparation are however the same as those used in chloromethylation reactions. The reaction between 8-hydroxyquinoline and formaldehyde in hydrochloric acid solution was therefore investigated in order to discover the reaction products formed under particular conditions, and to study the chelating properties of the substituted 8-hydroxyquinoline.

EXPERIMENTAL

Preparation of 7-chloromethyl-8-hydroxyquinoline hydrochloride

Formaldehyde (8 ml of a 37% solution) was added to a solution of 8-hydroxyquinoline in concentrated hydrochloric acid (7.3 g in 8 ml) and the resulting solution was saturated with hydrochloric acid gas for 2 to 3 hours. A bright yellow crystalline compound separated. Yield 60%. Calcd. for $C_{10}H_9NOCl_2$: C, 52.20; H, 3.95; Found: C, 51.98; H, 3.95; decomposes above 283 °C. 8-Hydroxyquinaldine could also be chloromethylated under the same conditions, and the product obtained was probably 7-chloromethyl-8-hydroxyquinaldine hydrochloride. Yield 58%. Calcd. for $C_{11}H_{11}NOCl_2$: C, 54.11; H, 4.54; Found: C, 53.85; H, 4.62.

Powder diffraction lines

For purposes of identification, X-radiograms of 7-chloromethyl-8-hydroxyquinoline hydrochloride and 7-chloromethyl-8-hydroxyquinaldine hydrochloride, were obtained by the powder diffraction method using a 11.483 cm diameter camera with Straumanis mounting and filtered copper $K\alpha$ radiation. The patterns were indicative of large unit cells with low symmetry. The interplanar distances of the twelve strongest lines for each compound are listed below.

8-Hydroxyquinoline compound

I/I_0	0.5	0.8	0.8	0.7	0.7	1.0	0.5	0.5	0.5	0.6	0.7	0.6
d	8.63	7.40	4.21	3.86	3.71	3.53	2.707	2.587	2.510	2.438	2.110	1.683

8-Hydroxyquinaldine compound

I/I_0	0.8	0.8	0.7	0.7	1.0	0.7	0.7	0.8	0.6	0.6	0.6	0.6
d	10.15	8.30	5.91	3.82	3.56	3.16	2.94	2.750	2.430	2.340	1.973	1.845

References p. 299

Preparation of 7-hydroxymethyl-8-hydroxyquinoline

An aqueous solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride was neutralized with 1 : 4 ammonia until the solution was distinctly alkaline to litmus. On standing for a few hours, a precipitate was obtained which was filtered and recrystallized from ethyl alcohol. Yield 45%. Calcd. for $C_{10}H_9NO_2$: C, 68.54; H, 5.18; N, 8.00; Found: C, 67.95; H, 5.10; N, 8.05; m.p. 123° C.

Preparation of 5-bromo-7-bromomethyl-8-hydroxyquinoline

Bromine was added dropwise and with rapid stirring to an aqueous solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride, until a precipitate was obtained, which was filtered and recrystallized from ethyl alcohol. Yield 55%. Calcd. for $C_{10}H_7NOBr_2$: C, 37.88; H, 2.23; N, 4.42; Found: C, 37.70; H, 2.19; N, 4.48; m.p. 192° C.

Qualitative and sensitivity tests

An aqueous 1% solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride was used for both the qualitative and sensitivity tests. 1% solutions of the following metal ions were used in these tests:

Co^{+2} , Fe^{+3} , Ni^{+2} , Cd^{+2} , Zn^{+2} , Cu^{+2} , Mn^{+2} , Bi^{+3} , Ag^{+} , Pb^{+2} , Al^{+3} , Ca^{+2} , Ba^{+2} , Mg^{+2} , Cr^{+3} , VO^{+2} and UO_2^{+2} .

DISCUSSION

When formaldehyde reacted with a hydrochloric acid solution of 8-hydroxyquinoline in the presence of hydrochloric acid gas, it was found that the hydrochloride of a chloromethyl derivative of 8-hydroxyquinoline was obtained. This compound is most probably 7-chloromethyl-8-hydroxyquinoline hydrochloride. Attempts to obtain the free base from this hydrochloride resulted in a partial or complete conversion of the chloromethyl group into a hydroxymethyl group. This indicated that the use of the chloromethyl derivative as an analytical reagent for metal ions would be limited to acid or neutral solutions. Bromination of 7-chloromethyl-8-hydroxyquinoline hydrochloride gave a dibromo compound instead of the expected monobromo derivative. This dibromo compound is probably 5-bromo-7-bromomethyl-8-hydroxyquinoline.

Qualitative tests were carried out with an aqueous solution of 7-chloromethyl-8-hydroxyquinoline hydrochloride. At pH 1.0 (dilute hydrochloric acid solution), Fe^{+3} and VO^{+2} ions formed green chelates. None of the other metal ions used gave a positive reaction at this pH. At pH 4.6 (acetic acid-acetate buffer), the following metal ions formed precipitates or colorations: Fe^{+3} , Co^{+2} , Ni^{+2} , Cd^{+2} , Zn^{+2} , Cu^{+2} , Mn^{+2} , Bi^{+3} , VO^{+2} , UO_2^{+2} , Ag^{+} and Pb^{+2} . The following metal ions did not react at pH 4.6: Al^{+3} , Ca^{+2} , Ba^{+2} , Mg^{+2} and Cr^{+3} .

The minimum concentrations of metal ions (in $\mu g/ml$), capable of reacting with the 7-chloromethyl-8-hydroxyquinoline hydrochloride, were determined by the method described by IRVING, BUTLER AND RING⁹. These minimum concentrations at pH 1.0 were: Fe^{+3} , 0.25; VO^{+2} , 0.16; and at pH 4.6 were: Co^{+2} , 5.8; Fe^{+3} , 0.8; Ni^{+2} , 5.8; Cd^{+2} , 5.8; Zn^{+2} , 6.6; Cu^{+2} , 4.2; Pb^{+2} , 5.8; VO^{+2} , 0.16; UO_2^{+2} , 2.5.

SUMMARY

The reaction of formaldehyde on a hydrochloric acid solution of 8-hydroxyquinoline, in the presence of hydrochloric acid gas, gave a chloromethyl derivative which is probably 7-chloromethyl-8-hydroxyquinoline hydrochloride. This compound is readily converted into the 7-hydroxymethyl derivative in alkaline solution. The 7-chloromethyl compound has been investigated as an analytical reagent for metal ions in acid solutions.

RÉSUMÉ

La réaction du formaldéhyde sur l'hydroxy-8 quinoléine en solution dans l'acide chlorhydrique, en présence d'acide chlorhydrique gazeux, donne un dérivé chlorométhylé, probablement le chlorhydrate de la chlorométhyl-7-hydroxy-8 quinoléine. Ce composé est rapidement transformé en dérivé 7-hydroxyméthylé, en solution alcaline. Le 7-chlorométhylcomposé a été examiné comme réactif analytique des cations, en solutions acides.

ZUSAMMENFASSUNG

Die Reaktion des Formaldehydes mit 8-Hydroxychinolin in salzsaurer Lösung in Gegenwart von gasförmiger Salzsäure, gibt ein Chloromethylderivat, wahrscheinlich das Hydrochlorid des 7-Chloromethyl-8-hydroxychinolins. Diese Verbindung wird in alkalischer Lösung schnell in das 7-Hydroxymethyl-Derivat übergeführt. Die 7-Chloromethylverbindung wurde in sauren Lösungen als analytisches Reagens für Kationen untersucht.

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OXIDATIONS WITH ALKALINE PERMANGANATE USING
MONOVALENT THALLIUM FOR THE BACK-TITRATION

III. ESTIMATION OF TRIVALENT ARSENIC

by

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In estimating arsenite with alkaline permanganate, STAMM¹ and HEREDIA², mix the solution with an excess of permanganate in alkaline medium, and titrate back the excess of oxidant with formate. Formate reduces permanganate to the manganate^{3,4} state and the accuracy of such a process necessitates that reduction of permanganate by the material to be estimated should not go further than that stage. Whether or not this is the case depends much on the alkali concentration, the reducing power of the material under investigation and the amount of Ba^{+2} present. The means of establishing conditions favouring a quantitative reaction is found by studying the reaction between $KMnO_4$ and arsenite. Difficulties are further overcome by carrying out the reduction of MnO_4^{-2} to Mn^{+4} in presence of telluric acid using monovalent thallium⁵ for back-titrating excess permanganate.

EXPERIMENTAL

The experimental technique and the preparation of permanganate solutions is essentially the same as described previously⁴.

The arsenite solutions were prepared by dissolving the c.p. product in twice-distilled water. The arsenite content was estimated by bromate, both volumetrically and potentiometrically^{6,7}.

The reaction between permanganate and arsenite as studied in this paper consists in the reduction of $KMnO_4$ with AsO_3^{-3} :

- (a) in absence of Ba^{+2} ions
- (b) in presence of telluric acid, and
- (c) in presence of Ba^{+2} ions.

The estimation of arsenic is further carried out by mixing the arsenite solution to a sufficient quantity of $KMnO_4$ under the proper conditions, followed by titrating excess oxidant with monovalent thallium.

RESULTS

I. Reduction of $KMnO_4$ in absence of Ba^{+2} ions

Reduction of MnO_4^{-} ions with arsenite leads to the formation of MnO_2 without any sign of formation of manganate even at the higher alkalinities; this is seen also in the disappearance of the inflection corresponding to manganate. This is apparently due to the strong reducing power of arsenite in alkaline medium. The redox potential of the AsO_4^{-3}/AsO_3^{-3} couple at unit OH^{-} amounts to -0.67 volt as compared with

0.588 volt for the $\text{MnO}_4^-/\text{MnO}_2$ system⁸. From these potential values, the equilibrium constant of the reaction and its degree of completion amounts to $1 \cdot 10^{-128}$ and $2.6 \cdot 10^{-26}$ respectively.

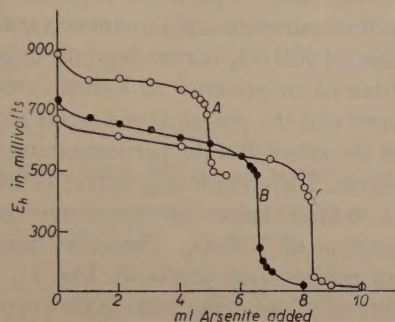


Fig. 1. (A) Titration of 10 ml 0.1266*N* KMnO_4 in 1*N* NaOH with 0.051*N* NaAsO_2 in presence of Ba^{+2} ions.
 (B) Titration of 10 ml 0.0555*N* KMnO_4 in 1*N* NaOH with 0.051*N* NaAsO_2 in the absence of Ba^{+2} ions and telluric acid.
 (C) Titration of 10 ml 0.1422*N* KMnO_4 in 2*N* NaOH with 0.102*N* NaAsO_2 in presence of telluric acid.

TABLE I

TITRATION OF KMnO_4 WITH SOD. META-ARSENITE IN ABSENCE OF TELLURIC ACID AND BARIUM IONS

<i>NaOH</i>	Max. inflec. per 0.1 ml arsenite <i>mV</i>	Theor. end-point <i>ml</i>	Exptl. end-point <i>ml</i>	Error %
Titration of 10.0 ml 0.1266 <i>N</i> KMnO_4 with 0.102 <i>N</i> NaAsO_2 :				
0.1 <i>N</i>	164	7.45	7.87	5.64
0.5 <i>N</i>	201	7.45	7.55	1.39
1 <i>N</i>	104	7.45	7.52	0.94
2 <i>N</i>	136	7.45	7.43	-0.27
3 <i>N</i>	89	7.45	7.42	-0.40
3.5 <i>N</i>	58	7.45	7.20	-3.35
Titration of 5.0 ml 0.02532 <i>N</i> KMnO_4 with 0.0102 <i>N</i> NaAsO_2 :				
2 <i>N</i>	137	7.45	7.35	-1.34
2.5 <i>N</i>	116	7.45	7.10	-4.70
Titration of 10.0 ml 0.01111 <i>N</i> KMnO_4 with 0.0102 <i>N</i> NaAsO_2 :				
0.5 <i>N</i>	182	6.54	6.63	1.37
0.7 <i>N</i>	132	6.54	6.56	0.31
1 <i>N</i>	182	6.5	6.30	-3.67
Titration of 10.0 ml 0.0555 <i>N</i> KMnO_4 with 0.051 <i>N</i> NaAsO_2 :				
0.5 <i>N</i>	216	6.54	6.50	-0.61
1 <i>N</i>	243	6.54	6.57	0.46
1.5 <i>N</i>	150	6.54	6.52	-0.30
Titration of 10.0 ml 0.0222 <i>N</i> KMnO_4 with 0.0204 <i>N</i> NaAsO_2 :				
0.5 <i>N</i>	200	6.54	6.62	1.22
1 <i>N</i>	266	6.54	6.54	nil
1.5 <i>N</i>	266	6.54	6.45	-1.37

The titration curves (curve C, Fig. 1) obtained under these conditions are smooth and characterized by sharp inflections at the MnO_2 stage, which coincide with the theoretical values in 2–3*N* NaOH. At lower alkalinities the end-points occur later than the theoretical, probably due to partial formation of Mn_2O_3 and the errors increase in magnitude on decreasing the alkali concentration. At alkalinities higher than 3*N* autodecomposition of KMnO_4 occurs leading to earlier end-points.

The best results are obtained in presence of telluric acid. In this latter case no manganese dioxide separates⁸ and the practical end-point coincides with the theoretical one irrespective of both the alkali and the permanganate concentration or the rate of adding the arsenite solution. The complexing action of telluric acid on manganese dioxide prevents reduction of Mn^{+7} below Mn^{+4} and overcomes the catalytic effect of MnO_2 on the decomposition of KMnO_4 . The inflections at the end-points are sharper than in absence of telluric acid (curve B, Fig. 1). As in absence of telluric acid no inflection was observed at the manganate state even at the highest alkalinity of 3*N*. In the presence and absence of telluric acid the reaction is rapid both at the beginning of the titration and at the end-point.

TABLE II

TITRATION OF KMnO_4 WITH SODIUM META-ARSENITE IN PRESENCE OF TELLURIC ACID AND ABSENCE OF BARIUM IONS

NaOH	Max. inflec. per 0.1 ml AsO_2^- mV	Theor. end-point ml	Exptl. end-point ml	Error %
Titration of 10.0 ml 0.1422 <i>N</i> KMnO_4 with 0.102 <i>N</i> NaAsO_2 :				
1.75 <i>N</i>	335	8.36	8.32	−0.48
2 <i>N</i>	258	8.36	8.33	−0.36
2.91 <i>N</i>	233	8.36	8.31	−0.60
Titration of 10.0 ml 0.01422 <i>N</i> KMnO_4 with 0.0102 <i>N</i> NaAsO_2 :				
1.5 <i>N</i>	71	8.36	8.33	−0.36

II. Reduction of KMnO_4 in presence of Ba^{+2} ions

Contrary to previous cases studied⁴, and obviously because of the strong reducing power of arsenite, reduction of KMnO_4 could not be easily checked at the manganate state by introducing Ba^{+2} ions. The equilibrium constants of the reaction occurring under these conditions and also the degree of completion are however smaller than those of the reactions performed in absence of Ba^{+2} ions. These values as calculated from the E'_0 values of the systems involved, viz.

$E'_0(\text{AsO}_4^{-3}/\text{AsO}_3^{-3}) = -0.67$ V and $E'_0(\text{MnO}_4^-/\text{MnO}_4^{-2}) = 0.56^8$,

amount to $1.7 \cdot 10^{-42}$ and $1.2 \cdot 10^{-14}$ respectively. Addition of an amount of Ba^{+2} equivalent to both arsenate and manganate formed in presence of 1*N* NaOH did not lead to an inflection at the manganate state. Further, the pink colour of permanganate remained visible even after the manganate inflection has been overstepped. However, by increasing the concentration of Ba^{+2} three or five-fold and decreasing the arsenite concentration

to 0.0255*N* and the permanganate to 0.05*N*, almost quantitative reduction could be obtained (curve A, Fig. 1). These difficulties render arsenite an unsuitable reagent for back-titrating permanganate in alkaline solution. This confirms the previous observations of HEREDIA² who prefers sodium formate to sodium arsenite. Further, although the reaction takes place rapidly at the beginning of the titration, it slows at the end-point, needing from 15-20 min for the attainment of equilibrium.

TABLE III
TITRATION OF KMnO_4 WITH NaAsO_2 IN PRESENCE OF BARIUM IONS

<i>NaOH</i>	5% Ba^{+2} <i>ml</i>	Max. inflec. per 0.1 ml AsO_2^- <i>mV</i>	Theor. end-point <i>ml</i>	Exptl. end-point <i>ml</i>	Error %
Titration of 10.0 ml 0.1422 <i>N</i> KMnO_4 with 0.102 <i>N</i> NaAsO_2 :					
0.5 <i>N</i>	excess	142	2.79	3.38	21.15
1.5 <i>N</i>	8	142	2.79	3.32	19.00
1.5 <i>N</i>	7	134	2.79	3.12	11.7
Titration of 10.0 ml 0.1422 <i>N</i> KMnO_4 with 0.0714 <i>N</i> NaAsO_2 :					
1 <i>N</i>	15	136	3.98	4.15	4.27
1.5 <i>N</i>	10	99	3.98	4.96	16.33
Titration of 10.0 ml 0.1261 <i>N</i> KMnO_4 with 0.051 <i>N</i> NaAsO_2 :					
1 <i>N</i>	9	82	4.94	4.97	0.60
1.5 <i>N</i>	10	150	4.94	4.96	-0.40
Titration of 5.0 ml 0.1261 <i>N</i> KMnO_4 with 0.0255 <i>N</i> NaAsO_2 :					
0.7 <i>N</i>	10	165	4.94	4.90	-0.81
Titration of 10.0 ml 0.0504 <i>N</i> KMnO_4 with 0.0255 <i>N</i> NaAsO_2 :					
0.7 <i>N</i>	10	180	3.95	3.94	-0.25
Titration of 10.0 ml 0.0504 <i>N</i> KMnO_4 with 0.0102 <i>N</i> NaAsO_2 :					
0.7 <i>N</i>	10	143	9.88	9.83	-0.51

III. Estimation of arsenite by oxidation with permanganate using monovalent thallium for titrating excess oxidant

As was previously shown, monovalent thallium can be used for back-titrating KMnO_4 in either the presence or absence of Ba^{+2} ions and in the presence of telluric acid⁵. We developed a method for the estimation of arsenic based upon these facts. Arsenite solutions are mixed with KMnO_4 , either in the presence of Ba^{+2} ions three times that equivalent to the arsenite and permanganate present and 1*N* NaOH , or in absence of Ba^{+2} ions and 1*N* to 2*N* NaOH . In both cases the arsenite is added dropwise and the excess KMnO_4 titrated with Tl^+ . In presence of Ba^{+2} ions KMnO_4 is reduced to permanganate whereas in their absence it is reduced to Mn^{+4} . Better

results, as can be seen from the data in Table IV, are obtained in this latter case. Small quantities of arsenic as low as 1 mg could be estimated with an accuracy of 0.5%.

TABLE IV
DETERMINATION OF As^{+3} USING Tl^{+} FOR BACK-TITRATING $KMnO_4$

Vol. & Normality of As^{+3} soln.	As added mg	As found mg	Error %
$KMnO_4 = 5.0$ ml $0.1111N$, $Tl^{+} = 0.0307N$, telluric acid present			
10 ml $\times 0.0102N$	3.820	3.805	-0.40
15 " "	5.730	5.720	-0.17
1 " "	0.382	0.381	-0.20
3 " "	1.146	1.140	-0.54
$KMnO_4 = 5$ ml $0.1132N$, $Tl^{+} = 0.0334N$			
5 ml $\times 0.0204N$	3.820	3.820	nil
10 " "	3.640	7.640	nil
0.5 " $\times 0.102N$	1.910	1.905	-0.24
1 " $\times 0.152N$	3.820	3.820	nil
2 " $\times 0.102N$	7.640	7.600	-0.50
Determination of As^{+3} using Tl^{+} for back-titration in presence of Ba^{+2} :			
1 ml $\times 0.0102N$	0.382	0.381	-0.20
5 " "	1.910	1.900	-0.50
2 " $\times 0.0204N$	1.528	1.528	nil
3 " "	2.292	2.291	-0.55

SUMMARY

In absence of Ba^{+2} ions arsenite reduces $KMnO_4$ in alkaline medium to MnO_2 without the appearance of an inflection at the manganate state. Reduction could be checked at the manganate in presence of $1N$ $NaOH$ and Ba^{+2} equal to 3 times that equivalent to MnO_4^{-2} and arsenate, and when dilute arsenite solutions are applied *viz.* $0.02N$. In absence of Ba^{+2} ions the end-points are attained later than the MnO_2 stage except in $2-3N$ $NaOH$. In presence of telluric acid good results are obtained at all alkalinities whence reduction is checked at Mn^{+4} .

As^{+3} could be estimated also by mixing with $KMnO_4$ either in the presence of Ba^{+2} ions + $1N$ $NaOH$ or in absence of Ba^{+2} ions + $1.5-3N$ $NaOH$ and back-titrating the excess oxidant with monovalent thallium.

RÉSUMÉ

En l'absence d'ions Ba^{+2} , l'arsenite en solution alcaline réduit $KMnO_4$ en MnO_2 sans qu'apparaisse le stade manganate. La réduction, en solution $0.02N$, peut s'arrêter au manganate en présence de $NaOH$ N et Ba^{+2} , en concentration égale à 3 fois celle de MnO_4^{-2} . En l'absence de Ba^{+2} , les points finals sont obtenus après le stade MnO_2 sauf dans $NaOH$ $2-3N$. En présence d'acide tellurique, la réduction en Mn^{+4} s'effectue à toutes les alcalinités. As^{+3} peut être dosé par $KMnO_4$, soit en présence de Ba^{+2} + $NaOH$ N , soit sans Ba^{+2} , dans $NaOH$ $1.5-3N$; l'excès d'oxydant est ensuite titré avec Tl^{+} .

ZUSAMMENFASSUNG

Bei Abwesenheit von Ba^{+2} Ionen, reduziert Arsenit in alkalischer Lösung $KMnO_4$ zu MnO_2 , ohne dass das Manganat-Stadium in Erscheinung tritt. In $0.02N$ Lösung, kann die Reduktion in Gegenwart von N $NaOH$ und Ba^{+2} in einer Konzentration die das Dreifache derjenigen des MnO_4^{-2} beträgt beim Manganat anhalten. Bei Abwesenheit von Ba^{+2} werden die Endpunkte nach

dem MnO_2 Stadium erhalten, ausser in 2-3N NaOH. In Gegenwart von Tellursäure, ist die Reduktion zu Mn^{+4} bei allen Alkalinitäten durchführbar. As^{+3} kann mit KMnO_4 bestimmt werden, sei es in Gegenwart von $\text{Ba}^{+2} + \text{N NaOH}$, sei es ohne Ba^{+2} , in 1.5-3N NaOH; der Überschuss des Oxydationsmittels wird darauf mit Ti^{+} titriert.

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5 : 6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT

I. DETERMINATION OF THORIUM AND ZIRCONIUM

by

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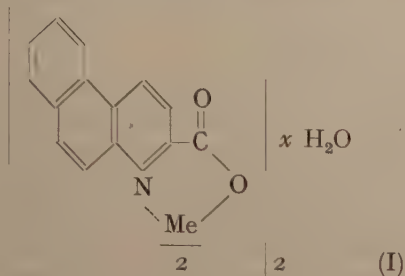
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The reagent, 5 : 6-benzoquinaldinic acid, m.p. 187° C, is highly soluble in alcohol and in acetic acid, less soluble in hot water and sparingly so in cold water. Under controlled pH conditions, it can be used to precipitate completely almost all the metals. Of them, copper gives a green precipitate; zinc, magnesium, calcium, strontium, barium, silver, mercury, lead and cadmium, white precipitates; cobalt, cream coloured; nickel, greenish and manganese, yellow.

The copper complex which is sparingly soluble in dilute mineral acids or acetic acid, is soluble in a large excess of ammonia and in solutions of alkali cyanide. All other complexes are more or less soluble in dilute acids. Such solubility in dilute acids is also shown by the complexes of iron(III), aluminium, antimony(III), bismuth, uranium (UO_2^{+2}), zirconium, thorium, beryllium, rare earths and tin(II), which are not precipitated from ammoniacal tartrate solutions. The chromic complex though soluble in ammoniacal tartrate medium is sparingly soluble even in fairly strong acids. Zinc, manganese, nickel, cobalt, silver, mercury and cadmium complexes are soluble in solutions of alkali cyanide and those due to lead and mercury also dissolve in an excess of ammonium acetate. The zinc complex is soluble also in an excess of ammonia, as is cadmium, and in alkali. Cobalt, nickel and manganese, on the other hand, are insoluble in ammonia. In moderately strong caustic soda solution both the nickel and manganese complexes are decomposed to their hydroxides, but that of cobalt, dissolves on heating and reappears on cooling. The lithium and thallous complexes are soluble in dilute acids and in hot water as are the complexes of beryllium, barium, calcium and strontium. Vanadate, molybdate and tungstate are not precipitated by the reagent from an alkaline solution, but in the presence of acid they give yellowish white precipitates which are sparingly soluble in excess of dilute acids. All the metal complexes, except that of beryllium, have been found to be insoluble in organic solvents such as ethyl and amyl alcohols, ether, chloroform, ethyl acetate, benzene, carbon disulphide and carbon tetrachloride. The beryllium complex on the other hand is fairly soluble in ethyl acetate and acetone and slightly so in ethyl alcohol and chloroform.

The pH regions for complete precipitation of copper, cadmium, zinc, manganese, nickel and cobalt are respectively at and over 0.82, 3.12, 2.85, 2.90, 3.00 and 3.24. Even at a pH value of about 10 they may be accurately determined. Copper is com-

pletely precipitated even from cupro-ammonium salt solutions in the presence of an excess of ammonium salt. The complexes when dried at about 110°C are hydrated and may be represented by (I).



Where Me is a bivalent metal cation

They dehydrate at higher temperatures, *e.g.*, the copper complex becomes anhydrous at 168°C , cadmium at 130°C , zinc at 186°C , cobalt at 150°C , while at 180°C nickel and manganese lose 7.23% and 6.60% of water respectively. The degree of hydration is independent of the pH except in the case of cadmium where the highly crystalline hydrated complex precipitated at a pH lower than 3.85, contains 1.5 moles of water, but when precipitated at a higher pH it retains water to the extent of about 2 moles, which is eliminated only at temperatures above 165°C . This retention of extra water is due perhaps to the nature of the precipitate.

Recently it has been observed that the mercury complex, like that of silver, is anhydrous at 100°C and stable up to 150°C ; it is completely precipitated over the pH range 1.9 to 6.0. By the proper control of pH and by the help of a complexing agent it is easily separated from quite a large number of elements².

Of the three reagents, α -picolinic acid³, quinaldinic acid⁴ and 5:6-benzoquinaldinic



acid⁵ having the same functional groups = N — and —C — OH, ortho to each other, the salts of quinaldinic acid are less soluble than those of α -picolinic acid but far more soluble than those of 5:6-benzoquinaldinic acid owing to the weighting effect. As expected, the ferrous salt of α -picolinic acid in solution is highly soluble and stable but the ferrous salts of the other two acids are less stable and far less soluble. Here the stability of the ferrous salt in solution decreases with the increase in the molecular weight of the reagent. Thus the ferrous picolinate complex could not be isolated from water or alcoholic solution in which it is highly soluble, whereas the ferrous salts of the other two reagents easily separate from aqueous solutions and the ferrous picolinate is stable even at a pH of 6.7; the other ferrous salts are easily decomposed at that pH. Here it must be stated that neither great stability nor pronounced solubility in organic solvents is necessarily a characteristic feature of inner complex salts as is often erroneously assumed¹. Alkali cyanide, because it forms complexes of the type $[\text{Fe}(\text{org})_2(\text{CN})_2] \text{K}_2$ (where H org is the acid organic reagent) with the ferrous salts of these reagents^{3,4,5}, dissolves the ferrous complexes and besides intensification of the colour, stabilizes the colour system so formed. With 5:6-benzoquinaldinic acid, the region of maximum absorption is at $515 \text{ m}\mu$ and the colour intensity varies with the concentration of ferrous ion.

In previous communications, it was shown that 5:6-benzoquinaldinic acid could

be used for the separation and determination of copper and cadmium^{6,7}. Also the reagent was found to be effective for the estimation of zinc, cobalt, nickel and manganese⁸ and for the separation of copper and cadmium from various elements^{9,10}. The subject matter of the present investigation is the use of the reagent for the determination of thorium and zirconium and their separation from rare earths, alkaline earths and magnesium.

Thorium and zirconium are precipitated in weakly acid solution by 5:6-benzoquinaldinic acid; the precipitation of thorium and zirconium being complete above pH 3.0 and 1.8 respectively. The thorium compound is anhydrous when dried at 110° C and of composition $\text{Th}(\text{C}_{14}\text{H}_8\text{O}_2\text{N})_4$, but zirconium gives a compound of variable composition and so zirconium precipitates were always ignited to the oxide. The thorium precipitate, on the other hand, was either ignited to the oxide or weighed as $\text{Th}(\text{C}_{14}\text{H}_8\text{O}_2\text{N})_4$ after successive washings with water, alcohol and acetone.

Separation of thorium and zirconium from the rare earths can be carried out by simple precipitation from acid solution, and separation from magnesium and alkaline earths can be achieved from solutions containing ammonium salts.

EXPERIMENTAL

Reagents and apparatus

5:6-benzoquinaldinic acid was prepared according to the modified method of MAJUMDAR AND MALLICK⁶ and purified by recrystallization from glacial acetic acid. A 1%, alcoholic solution of the reagent of m.p. 187° C was used as precipitant.

Solutions of the rare earths were prepared from a thorium-free rare earth mixture prepared from monazite. All other chemicals used were of reagent grade and the strengths of the solutions of thorium, zirconium, rare earth mixture, strontium, barium and magnesium were determined by standard gravimetric procedures. Calcium was determined volumetrically. pH measurements were made with a bench model pH meter.

Composition of the thorium and zirconium salt of the reagent

An alcoholic solution of the reagent was added dropwise to acid solutions of thorium and zirconium until the precipitation was complete. The precipitates were then washed several times with hot water and then with hot alcohol to free them from excess reagent. The precipitates were dried at 110° C until their weights were constant. Weighed amounts of precipitates were ignited to the oxide. Thus the thorium compound was found to have the composition $\text{Th}(\text{C}_{14}\text{H}_8\text{O}_2\text{N})_4$ (% ThO_2 calc., 23.54; found, 23.50, 23.52) and stable even at 150° C. The zirconium complex was found to vary in composition from sample to sample.

Procedure

Acid solutions of thorium or zirconium after dilution to about 200 ml were adjusted to the desired pH and heated to boiling. To this hot solution was added, with stirring dropwise, the reagent solution until precipitation was complete. The solution was then kept on a hot-plate for about fifteen minutes, filtered, washed with hot 1% ammonium nitrate solution, dried, ignited and weighed (see Tables I and II).

For direct weighing of thorium as $\text{Th}(\text{C}_{14}\text{H}_8\text{O}_2\text{N})_4$, the thorium complex, after precipitation and digestion, was filtered through a weighed Gooch crucible, washed with hot water, then with hot alcohol and finally thrice with acetone. It was then dried at 110° C and weighed (see Table III). The method of direct weighing has the disadvantage that a thorough washing with hot water and hot alcohol blocks the pores of the crucible pad.

Separation of thorium from rare earths

Phosphate-free acid solution containing thorium and the rare earths with cerium in the trivalent state, rendered so by hydrogen peroxide, was diluted to about 250 ml, the pH adjusted to the yellow colour of methyl orange and heated to boiling. The thorium was precipitated with stirring by the dropwise addition of the reagent. After complete precipitation and digestion for about ten minutes followed the usual procedure referred to above (see Table IV).

Separation of zirconium from rare earths was carried out in the same way as for thorium, cresol red being used as indicator instead of methyl orange (see Table V).

Separation from alkaline earths and magnesium was effected according to procedures for the separation from the rare earths with the previous addition of about 5 g of ammonium chloride to the solution (see Table VI).

TABLE I
DETERMINATION OF THORIUM

ThO_2 present mg	pH	ThO_2 found mg	Error mg
71.4	4.3	71.3	-0.1
71.4	4.0	71.5	+0.1
71.4	3.8	71.4	0.0
71.4	3.4	71.2	-0.2
71.4	3.0	71.3	-0.1
71.4	2.5	70.2	-1.2

TABLE II
DETERMINATION OF ZIRCONIUM

ZrO_2 present mg	pH	ZrO_2 found mg	Error mg
26.5	3.0	26.6	+0.1
26.5	2.8	26.5	0.0
26.5	1.8	26.7	+0.2

pH values less than 1.8 give a non-crystalline precipitate.

TABLE III

ThO_2 present mg	Th -compound mg	ThO_2 found mg
27.6	119.0	27.9
27.6	118.6	27.8
27.6	118.6	27.8

TABLE IV
SEPARATION OF THORIUM FROM RARE EARTHS

ThO_2 present mg	R_2O_3 present mg	ThO_2 found mg	Error mg
71.4	101.2	71.5	+0.1
71.4	202.4	71.3	-0.1
35.7	50.6	35.6	-0.1
27.6	375	27.5	-0.1
27.6	375	27.7	+0.1

TABLE V
SEPARATION OF ZIRCONIUM FROM RARE EARTHS

ZrO_2 present mg	R_2O_3 present mg	ZrO_2 found mg	Error mg
26.5	37.5	26.5	0.0
26.5	37.5	26.6	+0.1
26.5	375	26.6	+0.1
26.5	375	26.4	-0.1

TABLE VI

SEPARATION OF THORIUM AND ZIRCONIUM FROM MAGNESIUM AND ALKALINE EARTHS

ThO ₂ present mg	Ion added mg	ThO ₂ found mg	Error mg
27.6	Ca-100 R ₂ O ₃ -187.5	27.9	+0.3
27.6	Mg-100 R ₂ O ₃ -187.5	27.7	+0.1
27.6	Ca-100	27.5	-0.1
27.6	Ba-100	27.6	0.0
27.6	Sr-100	27.7	+0.1
ZrO ₂ present mg		ZrO ₂ found mg	
26.5	Ca-100	26.4	-0.1
26.5	Mg-100	26.7	+0.2
26.5	Ba-100	26.6	+0.1
26.5	Sr-100	26.5	0.0

Further work of this nature is in progress.

SUMMARY

Thorium and zirconium are determined in the presence of rare earths, alkaline earths and magnesium, when precipitated from weakly acid solution with 5:6-benzoquinaldinic acid. Thorium is completely precipitated at pH 3.0 as $\text{Th}(\text{C}_{14}\text{H}_8\text{O}_2\text{N})_4$, but though zirconium is precipitated at the lower pH of 1.8, its composition is not stoichiometric and hence is ignited to the oxide before weighing. Co-precipitation of magnesium and alkaline earths is prevented by the addition of ammonium chloride.

RÉSUMÉ

Le thorium et le zirconium peuvent être dosés, en présence des éléments des terres rares, alcalino-terreux et du magnésium, par précipitation en solution faiblement acide, au moyen de l'acide 5,6-benzoquinaldinique. Le thorium précipite quantitativement au pH 3.0, sous forme de $\text{Th}(\text{C}_{14}\text{H}_8\text{O}_2\text{N})_4$, tandis que le zirconium précipite au pH 1.8, pour donner un corps de composition mal définie. Il faut le calciner en oxyde avant d'effectuer la pesée. La coprécipitation du magnésium et des éléments alcalino-terreux est empêchée par addition de chlorure d'ammonium.

ZUSAMMENFASSUNG

Das Thorium und das Zirkonium können in Gegenwart von seltenen Erden, Erdalkalien und Magnesium bestimmt werden, mittels einer Fällung in schwachsaure Lösung mit Hilfe von 5,6-Benzochinaldinsäure. Das Thorium fällt quantitativ bei pH 3.0 in Form von $\text{Th}(\text{C}_{14}\text{H}_8\text{O}_2\text{N})_4$ aus, während das Zirkonium bei pH 1.8 in Form einer Verbindung ausfällt, deren Zusammensetzung nicht stöchiometrisch ist. Vor dem Wägen muss man diese zu Oxyd kalinieren. Die Kopräzipitation von Magnesium und den Erdalkalien wird durch eine Zugabe von Ammoniumchlorid verhindert.

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MÉTHODE DE DOSAGE DU NICKEL MÉTALLIQUE EN PRÉSENCE DE COMPOSÉS OXYDÉS DE NICKEL DANS DES MATIÈRES COMPLEXES (MINÉRAIS)

par

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I. INTRODUCTION — OBJET DU PRÉSENT TRAVAIL

L'étude des possibilités de traitement métallurgique d'un minerai oxydé pauvre de nickel ayant fait apparaître qu'un procédé en deux stades (réduction du nickel à l'état métallique, puis formation de nickel-carbonyle à décomposer ultérieurement) pouvait être envisagé, il était indispensable que les deux stades opératoires fussent contrôlés séparément.

Le contrôle des résultats expérimentaux obtenus au premier stade (réduction des composés oxydés de nickel en nickel métallique) exigeait les déterminations quantitatives du nickel oxydé et du nickel métallique dans un même échantillon.

Il était impossible d'atteindre ce but en dosant le nickel total, puis l'oxygène contenu dans les oxydes de Ni, de nombreux composés oxydés autres que ceux de Ni étant présents dans la matière étudiée en proportions variables suivant le degré de réduction.

Des recherches bibliographiques poussées ne nous ont fourni aucune indication précise et nous avons dû, dans ces conditions, essayer de mettre au point une méthode d'analyse permettant de doser séparément, dans un minerai complexe, le nickel métallique d'une part, et le nickel dans l'ensemble de ses combinaisons oxydées (oxydes, silicates) d'autre part.

Le problème a été résolu en déterminant dans quelles conditions il est possible de mettre en solution la totalité du nickel métallique en laissant inaltérés tous les composés oxydés de Ni. On dose alors le nickel total et le nickel mis sélectivement en solution dans ces conditions, et par différence, on obtient le nickel présent sous forme oxydée.

Divers essais de mise en solution sélective du nickel métallique dans différents milieux ont échoué. Ils ont néanmoins été utiles en faisant apparaître des différences marquées dans les vitesses de mise en solution du nickel métallique d'une part (dissolution rapide) et des composés oxydés de nickel d'autre part (dissolution très lente). Malheureusement, la vitesse de dissolution du nickel métallique diminue très rapidement au fur et à mesure de l'abaissement de sa teneur dans les solides résiduels, et la dissolution complète du nickel métallique n'a jamais pu être atteinte sans qu'une

fraction plus ou moins importante, mais jamais négligeable, du nickel oxydé entrât aussi en solution.

Les divers milieux dissolvants essayés ont montré l'influence primordiale de la durée de l'opération, qui doit être assez importante pour que tout le nickel métallique soit mis en solution. Il était donc obligatoire de ne retenir que ceux qui, après des actions de longue durée, ne permettaient rigoureusement aucune mise en solution du nickel oxydé.

Il apparut assez rapidement qu'un milieu remplissant assez bien ces conditions était une solution de chlorure mercurique. Des recherches systématiques ont permis de préciser la nature exacte de la solution à utiliser et les conditions de son emploi.

Au cours de ces recherches, diverses modifications ont été apportées à la solution de chlorure mercurique. Le but poursuivi était surtout l'obtention d'une méthode donnant plus rapidement des résultats suffisamment exacts. En particulier, le pH de la solution a été augmenté par addition d'un complexant du mercure, pour éviter sa précipitation. Le complexant choisi a été le cyanure de potassium.

Les essais de mise en solution sélective du nickel métallique par la solution ainsi modifiée n'ont donné aucun résultat positif. Toutefois, en abaissant par addition d'acide chlorhydrique le pH d'une solution contenant du chlorure de mercure(II) et du cyanure de potassium, on a constaté qu'il était possible de dissoudre sélectivement le nickel métallique dans certaines conditions. Celles-ci ont été précisées et ont conduit à l'obtention d'une seconde méthode permettant de doser le nickel métallique en présence de ses combinaisons oxydées.

Dans le présent travail sont décrits succinctement:

- 1) Les résultats des essais ayant conduit à l'obtention de deux moyens de mise en solution sélective du nickel métallique;
- 2) Les méthodes d'analyse qui en ont été déduites;
- 3) La vérification de ces méthodes appliquées à des mélanges synthétiques d'abord, à des minerais complexes contenant une quantité connue de nickel métallique, ensuite.

II. DÉTERMINATION DES POSSIBILITÉS DE MISE EN SOLUTION SÉLECTIVE DU NICKEL MÉTALLIQUE

A. Produits utilisés

Le nickel métallique est de la poudre de nickel exempte de cobalt et obtenue par réduction par l'hydrogène. Cette poudre ayant pu s'oxyder légèrement pendant le stockage, elle a été chauffée pendant 1 heure 30 à 175-225° C dans un courant d'hydrogène¹.

L'oxyde de nickel est en réalité un mélange d'oxydes NiO et Ni₂O₃ en proportions non définies, l'essentiel étant l'absence absolue de nickel métallique. Le produit, qui sera appelé oxyde de nickel dans cette note, a été obtenu par calcination de Ni(NO₃)₂·6H₂O, de qualité *p.a.*, pendant 3 heures à 900° C, par porphyrisation en mortier d'agate, et par une nouvelle calcination de 2 heures à 900° C². Le produit final est conservé en exsiccateur.

Les autres réactifs, HgCl₂, KCN et HCl, sont tous des produits de qualité *p.a.*

B. Essais de dissolution du nickel métallique

1. Mode opératoire

Peser exactement 0.1000 à 0.1010 g de nickel en poudre. Porter à l'ébullition dans un vase conique surmonté d'un réfrigérant la solution étudiée. Dès que l'ébullition est franche, verser dans la solution la poudre de nickel et maintenir l'ébullition pendant une durée déterminée.

Laisser refroidir et filtrer. Dans le filtrat acidifié par HCl, précipiter le mercure par H₂S, filtrer, chasser H₂S du filtrat par ébullition prolongée et doser Ni par électrolyse en milieu ammoniacal³.

2. Influence de la durée et de la concentration en HgCl_2 de la solution

La première série d'essais a été effectuée avec des solutions dont la concentration en HgCl_2 était variable; leur pH variait naturellement en fonction de cette concentration. L'ébullition pendant des durées différentes a donné les résultats suivants:

<i>Solution utilisée</i>	<i>pH</i>	<i>Durée</i>	<i>% Ni dissous</i>
50 ml HgCl_2 à 37 g/l	3.4	15 min	88.0
50 ml HgCl_2 à 37 g/l	3.4	2h	97.1
50 ml HgCl_2 à 37 g/l	3.4	6h	98.2
50 ml HgCl_2 à 25 g/l	3.6	2h	97.6
50 ml HgCl_2 à 25 g/l	3.6	6h	100.0
50 ml HgCl_2 à 18.5 g/l	3.7	2h	95.0
50 ml HgCl_2 à 18.5 g/l	3.7	6h	99.0

Ces résultats montrent que la concentration en HgCl_2 de la solution n'a qu'une influence faible, si on la compare à celle de la durée de l'opération. De plus, on voit nettement que la vitesse de dissolution ralentit fortement lorsque la quantité de nickel métallique non encore attaqué est faible.

3. Influence de la durée de l'expérience et de la quantité de solution

Pour étudier le facteur „quantité de solution”, il a été décidé d'utiliser la solution à 18.5 g/l HgCl_2 . L'influence de la durée de l'expérience a été observée également. Les résultats ont été les suivants:

<i>Solution utilisée</i>	<i>pH</i>	<i>Durée</i>	<i>% Ni dissous</i>
75 ml HgCl_2 à 18.5 g/l	3.7	15 min	83.4
75 ml HgCl_2 à 18.5 g/l	3.7	2h	96.1
75 ml HgCl_2 à 18.5 g/l	3.7	6h	100.0
100 ml HgCl_2 à 18.5 g/l	3.7	15 min	93.0
100 ml HgCl_2 à 18.5 g/l	3.7	2h	100.0

En comparant ces résultats à ceux qui ont été obtenus avec 50 ml de solution (voir 2, ci-dessus), on peut observer que la dissolution totale de la quantité choisie arbitrairement (0.1000 g) de Ni métallique est d'autant plus rapide que le volume de solution employé est grand.

Les deux séries d'essais dont les résultats sont donnés ci-dessus permettent déjà d'affirmer que dans trois cas précis, il est possible de dissoudre 100 % du nickel métallique, lorsqu'on opère dans des conditions bien définies, soit une prise d'essai de 0.1 g de nickel en poudre et une attaque de 6 heures par 50 ml de solution à 25 g/l HgCl_2 ou 75 ml de solution à 18.5 g/l HgCl_2 ou attaque de 2 heures par 100 ml de solution à 18.5 g/l HgCl_2 .

La durée de l'attaque étant assez longue, nous avons essayé de réduire cette durée par divers moyens. La seule méthode suffisamment bien étudiée fut l'addition de cyanure de potassium à la solution de chlorure mercurique. De cette façon, il était possible de faire varier le pH de la solution en évitant toute précipitation du mercure. De plus, le cyanure pouvait éventuellement agir comme complexant, et du mercure, et du nickel.

4. Influence d'une addition de KCN à la solution mercurique

La solution de base utilisée dans cette série d'expériences était constituée par 100 ml de solution à 18.5 g/l HgCl_2 , auxquels on ajoutait la quantité de solution à 80 g/l KCN nécessaire pour atteindre le pH voulu.

Les résultats sont résumés ci-dessous:

pH de la solution utilisée	Durée de l'expérience	% Ni dissous
5.2	6h	99.2
6.0	6h	98.2
7.0	6h	33.2
9.0	6h	1.015
10.5	6h	0.625

Ces essais ont montré nettement qu'une élévation de pH réduisait dans des proportions très marquées le pourcentage de Ni dissous après 6 heures. Il est évident que cette voie ne pouvait être suivie pour obtenir le résultat cherché.

Cependant, on peut obtenir un pH plus élevé que le pH naturel de la solution de base en ajoutant du KCN jusqu'à pH 10.5 puis en abaissant le pH par addition de HCl. Cette méthode a fait l'objet de la série d'essais suivante.

5. Influence du pH d'une solution contenant à la fois HgCl_2 , KCN et HCl

La solution de base utilisée dans cette série d'essais était constituée par 100 ml de solution à 18.5 g/l HgCl_2 et 25 ml de solution à 80 g/l KCN. Le pH de cette solution est 10.7. Par addition de solution de HCl 6N, on obtient la solution de pH voulu.

Les résultats obtenus ont été les suivants:

pH de la solution utilisée	Durée de l'essai	% Ni dissous
4.0	6h	9.26
6.0	15 min	35.6
6.0	6h	47.6
7.0	2h	70.2
7.0	6h	89.7
9.0	2h	84.2
9.0	6h	100.0

Comme on peut le remarquer, l'influence du pH, dans les solutions étudiées, est prépondérante pour la détermination de la vitesse de dissolution. Les chiffres sont à comparer aux résultats des essais effectués en solution HgCl_2 -KCN. Il semble donc que l'addition de KCN ou de KCN + HCl a une influence très défavorable sur la dissolution de Ni aux pH faibles, tandis qu'aux pH élevés, on peut obtenir une dissolution presque complète dans tous les cas avec un maximum de 100 % pour la solution HgCl_2 -KCN-HCl de pH 9.

Mais on doit également remarquer que le but que l'on cherchait à atteindre, c'est-à-dire réduire la durée de l'attaque, n'a pu être approché.

C. Étude de la dissolution de l'oxyde de nickel

Les résultats acquis jusqu'à présent ont montré que dans des conditions bien définies, il est possible de dissoudre la totalité du nickel métallique. Ces perspectives

encourageantes nous ont incité à poursuivre les essais de mise au point de la méthode d'analyse cherchée.

Il était donc nécessaire de voir comment se comporterait l'oxyde de nickel dans les conditions qui ont permis de mettre en solution la totalité du nickel métallique.

1. Mode opératoire

Peser exactement 0.1272 à 0.1286 g d'oxyde de Ni (ce qui correspond à 0.100—0.1010 g Ni, le facteur théorique étant 0.786).
Opérer ensuite exactement comme dans le cas du nickel métallique.

2. Résultats des expériences

Les expériences de dissolution de l'oxyde de nickel ont été effectuées uniquement avec les solutions et dans les conditions qui ont permis de dissoudre la totalité du nickel métallique. Les résultats ont montré que l'oxyde de nickel ne passait absolument pas en solution lorsque la solution était constituée soit par 100 ml de HgCl₂ à 18.5 g/l, avec ébullition de 2 heures, soit par 100 ml de HgCl₂ à 18.5 g/l, 25 ml de KCN à 80 g/l et la quantité de HCl 6N nécessaire pour obtenir un pH égal à 9.0, avec ébullition de 6 heures.

Dans les autres cas, il passe en solution une quantité non négligeable d'oxyde de nickel.

III. MÉTHODES DE DOSAGE PROPOSÉES

Les résultats des essais exposés ci-dessus permettent de proposer les deux méthodes de dosage suivantes pour déterminer la teneur en Ni métallique de matières contenant des composés oxydés de ce métal:

1. Dans un vase conique de 300 ml, verser 100 ml de solution à 18.5 g/l HgCl₂. Porter à l'ébullition sous condenseur. Dès que la solution bout, y verser une prise d'essai du minerai exactement pesée et contenant au maximum 0.1 g de Ni métallique.
Maintenir à l'ébullition pendant 2 heures, puis laisser refroidir. Filtrer. Dans le filtrat, doser le nickel par électrolyse après séparation du mercure et des autres éléments éventuellement dissous⁴.
2. Observer le même mode opératoire, mais en utilisant une solution composée de 100 ml de HgCl₂ à 18.5 g/l, 25 ml de KCN à 80 g/l et amenée à pH 9 par addition de HCl 6N. Dans ce cas, il faudra maintenir l'ébullition pendant 6 heures.

IV. VÉRIFICATION DES DEUX MÉTHODES DE DOSAGE PROPOSÉES

A. Vérification sur des mélanges synthétiques nickel métallique-oxyde de nickel

1. Mode opératoire

La vérification des deux méthodes proposées ci-dessus a d'abord porté sur des mélanges synthétiques de nickel métallique et d'oxyde de nickel. La prise d'essai était un mélange de ces deux constituants en proportions variables, tel que la quantité totale de nickel contenu soit comprise entre 0.1000 et 0.1010 g.

2. Essais en solution de HgCl₂ à pH 3.7 - 2 heures

Prise d'essai	g Ni contenu	% Ni métal	% Ni métal dosé
0.0251 g Ni + 0.0954 g NiO	0.10018	20.85	20.32
0.0501 g Ni + 0.0639 g NiO	0.100325	43.9	42.4
0.0752 g Ni + 0.0321 g NiO	0.10043	70.0	68.3

3. Essais en solution de HgCl_2 , KCN et HCl à pH 9 - 6 heures

Prise d'essai	Ni contenu g	% Ni métallique contenu	dosé
0.0252 g Ni + 0.0957 g NiO	0.10042	20.85	21.08
0.0504 g Ni + 0.06365 g NiO	0.10043	44.2	44.25
0.0757 g Ni + 0.0320 g NiO	0.100852	70.25	67.6

4. Conclusions des essais

Les résultats ci-dessus montrent que le dosage de Ni métallique en présence d'oxydes de nickel est possible à environ 3 % près par les méthodes proposées. La précision semble être d'autant meilleure que la teneur en Ni métallique est faible, surtout pour la solution HgCl_2 -KCN-HCl à pH 9.

B. Vérification sur des mélanges minéral de nickel-nickel métallique

1. Conditions opératoires

Pour cette série d'essais, on a utilisé un minéral oxydé de nickel de composition suivante: Ni 1.72 %; Co 0.10 %; Fe 35.55 %; SiO_2 16.4 %; CaO 2.10 %; MgO 1.08 %; Al_2O_3 13.50 %; Cr 2.28 %; Mn 0.98 %.

Dans ce minéral, le nickel se trouve sous forme d'oxydes et de silicates, mais pas d'aluminate, comme l'a montré une analyse aux rayons X.

Au moyen des deux méthodes d'analyse proposées, il a été vérifié que la teneur en Ni métallique était nulle.

Les essais ont été effectués en mélangeant à ce minéral des quantités variables de nickel métallique en poudre; dans un des essais, on a également ajouté du fer métallique en poudre pour voir quelle pouvait être son influence sur la dissolution du nickel métallique.

2. Essais en solution de HgCl_2 à pH 3.7 - 2 heures

Prise d'essai	Ni contenu g	% Ni métallique contenu	dosé
1.0028 g minéral + 0.0066 g Ni	0.02385	0.654	0.652
1.0044 g minéral + 0.0227 g Ni	0.03998	2.210	2.079
1.0021 g minéral + 0.0139 g Ni + 0.0136 g Fe	0.03114	1.350	1.311

3. Essais en solution de HgCl_2 , KCN et HCl à pH 9 - 6 heures

Prise d'essai	Ni contenu g	% Ni métallique contenu	dosé
1.0023 g minéral + 0.0074 g Ni	0.02464	0.733	0.743
1.0037 g minéral + 0.0219 g Ni	0.03916	2.135	2.092
1.0012 g minéral + 0.0140 g Ni + 0.0125 g Fe	0.03122	1.362	1.342

V. CONCLUSIONS

Comme le montrent les résultats expérimentaux exposés ci-dessus, les méthodes proposées pour le dosage du nickel métallique en présence de composés oxydés du nickel dans des matières complexes (minerais) permettent d'obtenir la teneur en

nickel métallique avec une erreur relative d'environ 5 %. La précision de l'analyse est meilleure quand la quantité de nickel métallique est faible; la présence éventuelle de fer métallique ne gêne pas.

La méthode utilisant une solution de HgCl_2 -KCN-HCl à pH 9 semble donner une précision un peu supérieure à celle obtenue par l'autre méthode, mais cet avantage est contrebalancé par une durée d'ébullition trois fois plus longue.

En conclusion, nous pouvons affirmer que la mise au point de ces deux méthodes nous a permis d'atteindre le but cherché.

RÉSUMÉ

Au cours de recherches sur le comportement du nickel métallique dans des milieux contenant HgCl_2 , KCN et HCl, on a remarqué que dans certains cas, la dissolution de nickel métallique était complète, alors qu'un mélange d'oxydes de nickel restait absolument inaltéré.

Les conditions opératoires ont été précisées et les résultats ont permis de mettre au point deux méthodes de dosage du nickel métallique en présence d'oxydes de nickel dans des matières complexes, y compris des minerais.

Ces méthodes sont décrites en détail et les résultats d'essais sont donnés; ils montrent qu'on peut obtenir une précision d'environ 5 %.

SUMMARY

During investigations on the behaviour of metallic nickel in HgCl_2 -, KCN- and HCl-containing media, it was noticed in certain cases that nickel metal dissolution was achieved, while a mixture of nickel oxides remained absolutely unaltered.

The working conditions were determined, and on the basis of the results obtained two methods have been developed for the determination of metallic nickel in the presence of nickel oxides in complex materials, including ores.

These methods are described in detail and the results of the experiments are given; they show that an accuracy of about 5 % can be obtained.

ZUSAMMENFASSUNG

Im Laufe der Untersuchungen über das Verhalten von metallischem Nickel in HgCl_2 -, KCN- und HCl-haltigen Lösungen wurde bemerkt, dass in gewissen Fällen die Au Lösung des metallischen Nickels vollständig war, während ein Nickeloxydgemisch ganz unverändert blieb.

Die Verfahrensbedingungen wurden genau bestimmt und die Ergebnisse haben erlaubt, zwei Analysemethoden des metallischen Nickels in Gegenwart von Nickeloxiden in komplizierten Stoffen, besonders in Erzen, aufzustellen.

Diese Methoden werden ausführlich beschrieben und die gefundenen Ergebnisse angeführt; sie zeigen dass eine Genauigkeit von 5 % erreicht werden kann.

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THE STORAGE OF SEA-WATER SAMPLES FOR THE DETERMINATION OF DISSOLVED INORGANIC PHOSPHATE

by

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A knowledge of the variation of the inorganic phosphate and total phosphorus content of sea-water is of considerable value to fishery chemists and marine biologists in the study of the fertility of the sea. In this connection several surveys of the phosphate concentration of surface waters and its relation to plankton and fish populations have been carried out. Although it is preferable to analyse sea-water samples immediately, this is not always possible. If such samples are stored without treatment, then the inorganic phosphate content of the water may be increased by the bacterial or enzymatic decomposition of the organic phosphorus of dead organisms, or decreased by its utilization by growing bacteria and plankton, or through adsorption on detritus.

A number of methods have been described for the preservation of sea-water samples for the determination of dissolved phosphate. IBANEZ¹ has recommended the addition of 1 ml of 1% sodium fluoride per 100 ml of sample. HARVEY² has suggested "baiting" the samples for determination of total phosphorus with freshly precipitated aluminium hydroxide, or preferably, with thorium carbonate, in an endeavour to adsorb epiphytic bacteria and organic matter so as to prevent them being adsorbed on the walls of the container; a few drops of chloroform were also added to prevent the proliferation of bacteria. The present work was carried out in an endeavour to find the optimum conditions for the preservation of samples to be analysed for inorganic phosphate.

EXPERIMENTAL

Samples of sea-water (chlorinity *ca.* 18.7⁰/₁₀₀) were filtered through a Whatman No. 1 filter paper, and then analysed for inorganic phosphate by HARVEY's molybdenum-blue method². They were then stored in the dark at *ca.* 20° in 150 ml swing-top soda glass bottles after the addition of various preservatives. After 28 days the samples were again analysed for phosphate.

(1) *No preservative*

Two water samples (13.5 and 25.7 $\mu\text{g PO}_4\text{-P/l}$) were each stored in two bottles with no added preservative and, after 1 month were found to contain 15.7 and 15.6, and 28.2 and 29.2 $\mu\text{g PO}_4\text{-P/l}$ respectively. This increase in the inorganic phosphate concentration is presumably due to bacterial or enzymatic hydrolysis of dissolved organic phosphorus compounds.

(2) *Sodium fluoride*

The fluoride ion inhibits the formation of molybdenum-blue. The addition of 1 ml and 2 ml of 1% sodium fluoride to 100 ml of sea-water containing 15 $\mu\text{g PO}_4\text{-P/l}$ reduced the optical density of the molybdenum-blue (measured at 705 $\text{m}\mu$) to 68.7% and 15.5% respectively of the optical density obtained in the absence of added fluoride. Since the presence of fluoride much reduces the sensitivity of the analytical method, the latter must be calibrated in the presence of the amount of fluoride used as a preservative. Three samples of sea-water (28.4 $\mu\text{g PO}_4\text{-P/l}$) to which 1 ml of sodium fluoride per 100 ml had been added, contained after one month, 23.0, 26.1 and 23.8 $\mu\text{g PO}_4\text{-P/l}$.

(3) *Aluminium hydroxide and thorium carbonate*

Attempts to use either aluminium hydroxide or thorium carbonate (up to 10 mg/150 ml) for the preservation of water samples led to very high and variable results.

(4) *Chloroform*

Three samples of sea-water (28.4 $\mu\text{g PO}_4\text{-P/l}$) preserved by the addition of 1 ml of chloroform per 150 ml, contained after 1 month 28.1, 28.5 and 28.5 $\mu\text{g PO}_4\text{-P/l}$.

It thus appears that of the preservatives tested only chloroform was satisfactory, and its effectiveness has been confirmed by further experiments. It should be stressed that all the present work was carried out using filtered sea-water, and it is recommended that all samples should be filtered⁴ immediately after collection. The specimens should be stored in the dark at as low a temperature as possible.

Use of polyethylene bottles for storage of sea-water samples

Polyethylene bottles are becoming quite widely used in oceanography for storage of water samples for silicate⁴ and trace element determinations, since they are light, robust and free from the possibility of contamination by silicon or trace metals. They may also be used for the short period storage of water specimens for chlorinity determinations⁵. Experiments were therefore carried out to test the possibility of using water stored in polyethylene bottles for phosphate determinations, and it was found that their use led to the disappearance in less than 6 days of almost all the inorganic phosphate from the water. That this disappearance was due to the adsorption of the phosphate ion by the polyethylene was shown by the fact that a polyethylene sheet, which had been shaken with sea-water containing 500 $\mu\text{g PO}_4\text{-P/l}$, liberated considerable amounts of phosphate ion when shaken with several portions of distilled water.

CONCLUSIONS

Samples of sea-water to be analysed for inorganic phosphate should be filtered⁴, and then stored in the dark after the addition of *ca.* 0.7 ml of chloroform per 100 ml of sample to inhibit bacterial action. Polyethylene bottles should not be used for the storage of samples to be analysed for phosphate since they adsorb phosphate ions strongly.

SUMMARY

A study has been made of methods of preservation of sea-water samples to be analysed for inorganic phosphate. It is recommended that the filtered samples be treated with 0.7 ml of chloroform per 100 ml of water and stored in the dark in glass bottles. Polyethylene bottles should not be used for water storage since they strongly adsorb phosphate ion.

RÉSUMÉ

Une étude a été effectuée sur les méthodes de préservation des échantillons d'eau de mer en vue de la détermination de leur teneur en phosphates inorganiques. Il est recommandé de traiter les échantillons filtrés par le chloroforme (0.7 ml CHCl_3 par 100 ml d'eau), et de les conserver dans l'obscurité dans des récipients en verre. Les flacons en polyéthylène ne doivent pas être utilisés pour la conservation de l'eau car ils adsorbent fortement les ions phosphoriques.

ZUSAMMENFASSUNG

Die Konservierungsmethoden von Meerwasserproben wurden im Hinblick auf die Bestimmung des Gehaltes an anorganischen Phosphaten untersucht. Es wird empfohlen die filtrierten Entnahmen mit Chloroform (0.7 ml CHCl_3 auf 100 ml Wasser) zu behandeln und sie in Glasgefäßen im Dunkeln aufzubewahren. Polyäthylenflaschen dürfen für die Aufbewahrung des Wassers nicht verwendet werden, da sie die Phosphationen stark adsorbieren.

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ÉTUDES SUR LA DÉTECTION, LA CARACTÉRISATION ET LE
DOSAGE DES ALDÉHYDES

I. MÉTHODES D'OXIMATION

par

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Parmi les méthodes proposées pour la détection et le dosage des aldéhydes, il faut sélectionner la ou les méthodes dont l'application semble être la plus universelle. Le réactif parfait serait celui qui précipiterait un aldéhyde quelconque, en formant un dérivé avec un point de fusion compris entre 50° et 200° par exemple, avec un rendement de 100 %, suffisamment stable pour être séché à poids constant. Un tel réactif permettrait à la fois la détection, la caractérisation et le dosage des aldéhydes.

Faute de ce réactif parfait, on peut essayer de trouver un composé, permettant par exemple le dosage par titrage, suivi de la séparation du dérivé obtenu, même si le rendement n'est pas de 100 %. L'oximation des aldéhydes a souvent été proposée. Ayant l'intention de faire une étude critique des diverses méthodes existantes, nous traiterons d'abord des méthodes d'oximation.

Parmi les procédés indiqués pour le dosage des aldéhydes par oximation, ceux recommandés par BRYANT ET SMITH¹, par WANKA, JUREČEK ET HOLÁNEK², par SMITH ET MITCHELL³, par JOHNSTON⁴ et par PERRET⁵ semblent être les mieux étudiés et de la plus grande universalité.

On constate que certains radicaux liés au groupement aldéhyde peuvent gêner le dosage, en empêchant une réaction complète entre l'aldéhyde et l'hydroxylamine, ou en ralentissant considérablement la réaction.

Une oximation incomplète peut être due à un „empêchement stérique”, causé par une ramification de la chaîne de carbone en position α par rapport au groupement aldéhydique. Un ralentissement de la vitesse de l'oximation peut être dû à la présence d'autres groupements dans la molécule, causant une déformation du système électronique du groupement aldéhyde.

Comme aldéhydes témoins, nous avons choisi les aldéhydes indiqués dans le Tableau I. Un empêchement stérique peut être prévu pour certains aldéhydes (I-IX), tandis que l'influence d'une déformation du système électronique peut être prévue parmi les numéros X-XIV.

Dans les Tableaux II et III, nous indiquons les poids moléculaires des aldéhydes examinés et les poids moléculaires que nous avons trouvés, en nous servant des 5 méthodes indiquées et en suivant les indications aussi rigoureusement que possible. D'après nos résultats, la méthode de SMITH ET BRYANT semble la plus universelle

TABLEAU I

ALDÉHYDES TÉMOINS POUR LES TITRATIONS

	Poids moléculaire
I. Paraformaldéhyde	30.0
II. Acétaldéhyde	44.0
III. Aldéhyde isobutyrique	72.1
IV. Aldéhyde triméthylacétique	86.1
V. Heptaldéhyde	114.2
VI. Benzaldéhyde	106.1
VII. <i>o</i> -Tolualdéhyde	120.1
VIII. <i>p</i> -Tolualdéhyde	120.1
IX. 2.6-Diméthylbenzaldéhyde	134.2
X. Furfural	96.0
XI. 2-Thiofénaldéhyde	112.1
XII. 2-Pyridylaldéhyde	107.1
XIII. 3-Pyridylaldéhyde	107.1
XIV. 4-Pyridylaldéhyde	107.1

TABLEAU II

TITRATION DES ALDÉHYDES TÉMOINS D'APRÈS DES MÉTHODES DIFFÉRENTES D'OXIMATION

Aldéhyde témoin	Méthode de BRYANT ET SMITH		Méthode de WANKA, JUREČEK ET HOLÁNEK	Méthode de SMITH ET MITCHELL	Méthode de JOHNSTON
	Électrode de verre	Électrode de platine	Électrode d'antimoine	pH 2.5	pH 3.0
I	30.1	—	30.3	33	33.1
II	—	—	42.5	45.2	44.7
II*	46.7	—	—	—	—
III	—	—	78.8	73.6	72.3
III*	72.2	—	—	72.3	—
IV	100.7	—	132.8	132	126.3
V	113.0	109.4	153.3	125	—
V*	—	—	—	118.8	120.0
VI	108.8	106.2	—	109.7	107.8
VI*	105.8	—	107.8	105.1	—
VII*	124.5	120.5	132.0	125	131.9
VIII*	119	134	127.3	120.7	123.8
IX*	190.5	—	392	271	236
X*	94.8	100	93.9	97.2	97.4
XI	112.5	—	119.0	118	130.4
XII	103.5	—	—	104.5	146.2
XII*	109.6	108.2	—	—	—
XIII	105.8	—	—	—	—
XIV*	106.4	110.2	—	—	—

* fraîchement distillé

TABLEAU III

TITRATION DU BENZALDÉHYDE ET DU FURFURAL D'APRÈS LA MÉTHODE DE PERRET

Minutes de repos	Poids moléculaires trouvés	
	Benzaldéhyde	Furfural
30	107.4	108.8
60	107.5	97.6
90	108.6	98.2
120	108.8	96.4
180	—	116.2

des méthodes examinées, mais même pour cette méthode nous avons trouvé des inexactitudes assez graves, dues partiellement à la détermination difficile du virage, le saut de potentiel n'étant pas suffisamment prononcé (voir Fig. 1).

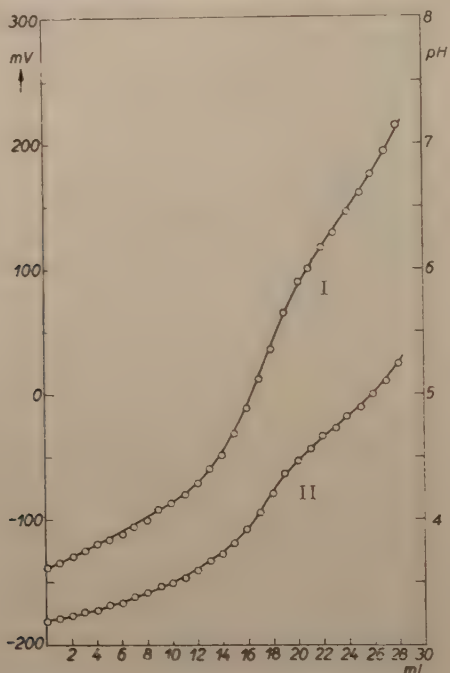


Fig. 1. Titration potentiométrique de l'oxime du furfural. Électrode de verre/Électrode au calomel
Courbe I: Ordonnée à droite (pH)
Courbe II: Ordonnée à gauche (mV).

Pour les méthodes où le point final de la titration est fixé au pH 2.5 ou pH 3.0, la présence dans la molécule d'un atome d'azote peut causer des inexactitudes (cas des pyridylaldéhydes) de même que la présence de l'hétéroatome soufre (2-thio-fénaldéhyde).

Quelques inexactitudes correspondant aux déviations prévues par un empêchement stérique sont observées en comparant les numéros II, III et IV, et les numéros VI, VII, VIII et IX.

De plus, il faut s'assurer que les aldéhydes sont tout à fait purifiés des produits de polymérisation ou d'oxydation (peroxydes ou acides), deux déterminations faites avec un intervalle de 24 heures donnant souvent des différences de plusieurs ‰.

PARTIE EXPÉRIMENTALE

*Méthode de BRYANT ET SMITH*¹. Nous avons suivi les indications des auteurs, échangeant toutefois la bouteille à pression avec un gobelet, et fixant le temps de repos, après addition de l'aldéhyde au réactif, à 2 heures. La titration visuelle a été abandonnée pour une titration potentiométrique, utilisant le système électrode de verre — électrode au calomel, ou électrode de platine — électrode au calomel. Pour ce dernier système, la fixation du virage a été extrêmement difficile, même en appliquant les méthodes recommandées par GRAY⁶ ou par SÖRENSEN⁷. JENSEN⁸, qui a comparé la méthode de SMITH ET BRYANT avec une détermination par réduction avec le borohydrure de sodium a eu les mêmes difficultés en fixant le virage (communication privée).

*Méthode de WANKA, JUREČEK ET HOLÁNEK*². Nous n'avons examiné que la titration en solution aqueuse. La précision de cette méthode n'est pas suffisante. Quatre déterminations simultanées de l'aldéhyde isobutyrique ont eu un écart trop grand. La substitution de l'hydroxylamine libre au chlorhydrate d'hydroxylamine n'a pas donné des résultats plus satisfaisants.

*Méthode de SMITH ET MITCHELL*³. Suivie rigoureusement, cette méthode nous a donné des résultats concordant avec les résultats indiqués par les auteurs. Un empêchement stérique est trouvé pour le triméthylacétaldéhyde, pour l'o-tolylaldéhyde et pour le 2,6-diméthylbenzal-déhyde. Une erreur causée par la présence d'un hétéroatome est trouvée pour le 2-thiofénaldéhyde et pour les pyridylaldéhydes, ces derniers étant trop basiques pour permettre une titration jus-qu'au pH 2.5.

*Méthode de JOHNSTON*⁴. Nous n'avons trouvé aucun avantage en substituant l'alcool butylique tertiaire à l'alcool éthylique.

*Méthode de PERRET*⁵. Nous n'avons examiné que quelques-uns des aldéhydes, trouvant qu'il faut déterminer pour chaque aldéhyde le temps de repos nécessaire pour terminer l'oximation (voir Tableau III).

Oximes nouvelles

Parmi les oximes de nos aldéhydes témoins, il y en a trois que nous n'avons pas trouvé men-tionnées dans la littérature et dont nous indiquons ici la préparation et les points de fusion.

Pour la préparation, nous nous sommes servis d'une méthode courante: 0.2 g de l'aldéhyde sont ajoutés à une solution de 0.5 g de chlorure d'hydroxylammonium dans 3 ml d'eau, puis 5-6 ml d'une solution de carbonate de sodium à 10 %. Le mélange est chauffé 10 minutes au bain-marie et refroidi dans l'eau glacée. Les oximes ne tardent pas à cristalliser, la cristallisation étant facilitée en grattant les parois avec une spatule. Ils sont ensuite recristallisés dans l'eau.

Dans le Tableau IV, nous indiquons les points de fusion et les analyses des oximes des pyri-dylaldéhydes -3 et -4 et de la 2,6-diméthylbenzaléhyde.

En préparant l'oxime de la 4-pyridylaldéhyde, nous avons obtenu deux modifications avec les points de fusion 121-122° et 133-133.5°. La modification à point de fusion le plus élevé représente la forme stable.

TABLEAU IV
POINTS DE FUSION ET ANALYSES DE QUELQUES OXIMES

Oxime de	Point de fusion		%C	%H	%N *)
3-Pyridylaldéhyde	146-146.5°	calculé	59.00	4.95	22.94
		trouvé	58.90	4.82	22.36
4-Pyridylaldéhyde	133-133.5°	calculé	59.00	4.95	22.94
		trouvé	59.20	4.95	22.70
	121-122°	calculé	59.00	4.95	22.94
		trouvé	59.30	5.07	22.40
2,6-Diméthylbenzaléhyde	158-159°	calculé	72.45	7.43	9.39
		trouvé	72.25	7.56	9.44

*) Microanalyses par M. PREBEN HANSEN, Laboratoire de l'Université de Copenhague.

Pour examiner s'il s'agit des formes *syn* et *anti* de l'oxime nous avons, d'après les indications de A. HANTZSCH⁹, traité les deux oximes par l'anhydride acétique froid, puis par une solution froide de carbonate de sodium. La solution alcaline est extraite par l'éther, la couche étherée est séparée et le solvant est évaporé. Le résidu est recristallisé dans l'essence de pétrole (point d'ébullition 60-100°). Les deux modifications ont donné une substance avec point de fusion 95-96°, que nous considérons comme l'acétate du 4-pyridylaldoxime:

$C_8H_8N_2O_2$ 164.2	calculé	C 58.53 %	H 4.91 %	N 17.07 %
	trouvé	C 59.15 %	H 5.21 %	N 17.22 %

L'acétylation semble être plus nette pour la substance avec point de fusion 133° que pour l'autre substance. Généralement c'est la forme *syn* qu'on peut acétyler, et l'expérience tend à indiquer, que les deux formes isolées sont des formes polymorphes, n'excluant tout de même pas complètement la possibilité d'une isomérisie géométrique.

REMERCIEMENTS

Nous tenons à remercier Statens almindelige Videnskabsfond et Otto Monsteds Fond pour des bourses qui ont permis à l'un de nous de prendre part au travail.

RÉSUMÉ

On a comparé 5 méthodes pour le dosage des aldéhydes par oximation. Pour toutes les méthodes, une ramification simple ou double, en position α pour les aldéhydes aliphatiques et en positions 2 et 6 pour les aldéhydes aromatiques tend à diminuer la précision des méthodes (empêchement stérique).

Parmi les méthodes examinées celles de BRYANT ET SMITH¹ et de SMITH ET MITCHELL³ sont les plus universelles.

Trois oximes nouvelles sont décrites. Pour l'une d'elles, deux modifications sont isolées, qui sont, toutes deux, transformées en acétate par l'action d'anhydride acétique et de carbonate de sodium. On discute s'il s'agit des formes *syn* et *anti* de l'oxime ou de deux modifications polymorphes.

SUMMARY

Five methods for the estimation of aldehydes by oximation have been compared. In all the methods, a single or double branching in position α in the case of aliphatic aldehydes, and in positions 2 and 6 in the case of aromatic aldehydes, tends to lessen the accuracy (steric hindrance). Of the methods examined those of BRYANT AND SMITH¹ and SMITH AND MITCHELL³ are the most common.

Three new oximes are described. For one of these, two modifications have been isolated, both of which are converted to acetate by the action of acetic anhydride and sodium carbonate. The question is discussed whether this is a case of the *syn* and *anti* forms of the oxime or of two polymorphic modifications.

ZUSAMMENFASSUNG

Es wurden 5 Methoden für die Bestimmung von Aldehyden durch Oximation verglichen. Für alle diese Methoden wirken Verzweigungen der Moleküle im Sinne einer Verminderung der Präzision (sterische Hinderung), und zwar eine einfache oder doppelte Verzweigung in α -Stellung für aliphatische Aldehyde und in 2 und 6 Stellung für die aromatischen Aldehyde. Von allen diesen geprüften Methoden sind die von BRYANT UND SMITH¹ und von SMITH UND MITCHELL³ die allgemeinsten.

Es werden drei neue Oxime beschrieben. Für eines von diesen wurden zwei Modifikationen isoliert, welche beide unter dem Einfluss von Essigsäureanhydrid und Natriumkarbonat in Acetate verwandelt werden. Die Frage wird erörtert ob es sich um die *syn*- und *anti*-Formen des Oximes oder um 2 polymorphe Modifikationen handelt.

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COMMENTS ON A MODIFIED TUTWILER METHOD FOR THE DETERMINATION OF H_2S AND SO_2 IN GASES

by

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INTRODUCTION

For controlling the operation of the well-known Claus sulphur recovery process, in which sulphur is obtained by the oxidation of hydrogen sulphide, a rapid method for analysing gases containing both H_2S and SO_2 is required.

Some years ago, a publication¹ appeared in which it was stated that the analysis could be carried out by a modification of Tutwiler's method² for determining H_2S . Since this modified form of the Tutwiler analysis has been adopted in industry, and the present author had occasion to find that its results are not reliable, this paper aims at showing its range of suitability and its shortcomings. At the end of the article reference will be made to an alternative analytical procedure developed by the author for carrying out this analysis.

The modified Tutwiler method consists in a titration of the total quantity of H_2S and SO_2 in a measured volume of gas with a standard iodine solution, in the presence of a neutral starch solution. This iodometric titration is followed by an acidimetric titration of the resulting hydriodic and sulphuric acids.

The simplicity of the method makes it particularly attractive for routine determinations. However, it is common knowledge that in aqueous media H_2S may react with SO_2 to form elementary sulphur and this reaction may also take place during the above determination. In order to investigate whether this method can nevertheless be used for the object in view, the experiments described below were carried out.

EXPERIMENTAL

When the Tutwiler method was employed for mixtures of H_2S in nitrogen, correct results were obtained in the iodometric titration. The acidimetric titration of the HI formed, however, gives low values (see Table I). This is probably due to oxidation of the HI.

When the Tutwiler method was applied to mixtures of SO_2 in nitrogen, both iodometric and acidimetric titrations gave low results. This fact is to be attributed to the loss of SO_2 during the introduction of the sample in the pipette, by solution in the outflowing starch solution. This is proved by the influence of the rate at which the starch solution is withdrawn from the pipette (see Table II, experiments 10 to 16).

TABLE I
 ANALYSIS OF H_2S/N_2 MIXTURES

Gas Sample	Expt. No.	Actual H_2S , % vol.	Experimental H_2S , % vol.			
			iodometric		acidimetric	
			% vol.	difference	% vol.	difference
I	1	17.40	17.00	-0.40	not determined	
	2	17.40	17.20	-0.20	16.20	-1.20
	3	17.40	17.50	+0.10	16.65	-0.75
	4	17.40	17.40	0.0	16.60	-0.80
	5	17.40	17.70	+0.30	14.50	-2.90
	6	17.40	17.80	+0.40	16.80	-0.60
	average	17.40	17.43	+0.03	16.15	-1.25
II	7	4.96	4.85	-0.11	4.69	-0.27
	8	4.96	4.82	-0.14	4.33	-0.63
	9	4.96	4.72	-0.24	4.57	-0.39
	average	4.96	4.80	-0.16	4.53	-0.43

 TABLE II
 ANALYSIS OF AN SO_2/N_2 MIXTURE

Expt. No.	Actual SO_2 , % vol.	Kerosine layer	Rate of withdrawal of starch solution	Experimental SO_2 , % vol.			
				iodometric		acidimetric	
				% vol.	difference	% vol.	difference
10	3.95	without	slow	2.61	-1.34	2.65	-1.30
11	3.95	"	moderate	3.16	-0.79	not determined	
12	3.95	"	"	3.04	-0.91	3.05	-0.90
13	3.95	"	"	2.98	-0.97	2.82	-1.13
14	3.95	"	"	3.32	-0.63	3.32	-0.63
15	3.95	"	"	3.20	-0.75	3.22	-0.73
16	3.95	"	fast	3.62	-0.33	3.63	-0.32
17	3.95	with	slow	3.89	-0.06	3.71	-0.24
18	3.95	"	moderate	3.95	0.0	not determined	
19	3.95	"	"	3.96	+0.01	3.87	-0.08
20	3.95	"	"	3.83	-0.12	3.95	0.0
21	3.95	"	fast	3.92	-0.03	3.83	-0.12

A considerable improvement was effected by placing a thin layer of kerosine on the starch solution, so as to reduce the rate of solution of SO_2 in the starch solution (see Table II, experiments 17 to 21).

Gases containing both H_2S and SO_2 in nitrogen gave very erratic results (see Table III). A considerable amount of elementary sulphur was formed during the introduction of the gas as a result of the reaction between H_2S and SO_2 , even when employing a kerosine layer on the starch solution.

An attempt was then made to eliminate the use of aqueous solution as confining liquid during the sampling. An evacuated dry pipette was filled with gas, whereupon a measured quantity of the standard iodine solution was admitted and the excess was titrated back in the liquid, after withdrawing the latter from the pipette, with sodium thiosulphate. Though this procedure led to better results (see experiments 28 to 30), it is less simple and consequently unattractive.

Summarizing, we can state that the modified Tutwiler method can be used for the determination of H_2S or of SO_2 alone, but not for gases containing both components.

TABLE III
 ANALYSIS OF AN $\text{H}_2\text{S}/\text{SO}_2/\text{N}_2$ MIXTURE

Expt. No.	Procedure	Actual H_2S % vol.	Actual SO_2 % vol.	H_2S found experimentally		SO_2 found experimentally	
				% vol.	Diff.	% vol.	Diff.
22	with kerosine film	2.40	4.21	0.72	-1.68	2.71	-1.50
23	"	2.40	4.21	0.75	-1.65	3.02	-1.19
24	"	2.40	4.21	0.84	-1.56	3.38	-0.83
25	"	2.40	4.21	0.41	-1.99	3.34	-0.87
26	"	2.40	4.21	0.78	-1.62	3.33	-0.88
27	"	2.40	4.21	1.29	-1.11	3.48	-0.73
28	dry pipette	2.40	4.21	2.43	+0.03	4.51	+0.30
29	"	2.40	4.21	2.11	-0.29	4.49	+0.28
30	"	2.40	4.21	1.95	-0.45	4.57	+0.36

The present author, together with F. VAN DE CRAATS, recently published³ another analytical method for the same purpose, which does not suffer from the above-mentioned disadvantages. It is based on the selective oxidation of H_2S and SO_2 in H_2O_2 solutions.

The gas to be analysed is passed through two washing-bottles, one filled with a neutral (or slightly acid) and one with an alkaline H_2O_2 solution. The SO_2 is oxidized in the former solution, the H_2S in the latter. The separation between the gases is completed by stripping the solutions with air. Subsequently the sulphuric acid formed in each washing bottle is titrated to the methyl red end-point.

Some determinations by the latter method on a synthetic mixture of H_2S , SO_2 and N_2 are given in Table IV.

TABLE IV

ANALYSIS OF A MIXTURE OF H_2S (2.10% VOL.), SO_2 (4.40% VOL.) AND N_2 (REMAINDER) BY THE H_2O_2 METHOD³.

H_2S (% vol.)		SO_2 (% vol.)	
Found	Diff.	Found	Diff.
2.15	+0.05	4.43	+0.03
2.10	—	4.27	-0.13
2.10	—	4.38	-0.02
2.13	+0.03	4.42	+0.02

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SUMMARY

A modified form of the Tutwiler analysis which was proposed a few years ago and has to some extent, been used as a method for controlling the Claus sulphur recovery process, has been examined as to its exactitude for this purpose, *viz.*, for determining both H_2S and SO_2 in gas mixtures.

It has been found suitable for the determination of H_2S alone, and also (with a small modification) of SO_2 alone, but not for both compounds if they occur together.

These disadvantages are not possessed by an alternative method of analysis, recently published.

RÉSUMÉ

Une forme modifiée de l'analyse selon Tutwiler a été proposée il y a quelques années et employée dans quelques cas isolés pour le contrôle du procédé Claus de récupération du soufre. Une étude a été faite pour en examiner le degré d'exactitude dans cette application, c.à.d. pour la détermination de H_2S et de SO_2 dans des mélanges gazeux.

Il a été trouvé que la méthode se prête bien à la détermination de H_2S seul et, avec une légère modification, de SO_2 seul, mais non à celle des deux substances si elles sont présentes en même temps.

Une autre méthode d'analyse récemment publiée ne présente pas ce désavantage.

ZUSAMMENFASSUNG

Eine geänderte Form der Tutwiler Analyse, die vor einigen Jahren als Methode zur Kontrolle des Claus-Verfahrens zur Zurückgewinnung von Schwefel vorgeschlagen wurde und in einzelnen Fällen benutzt worden ist, wurde auf ihre Genauigkeit für diesen Zweck, d.h. für die Bestimmung von H_2S und SO_2 in Gasgemischen geprüft.

Es stellte sich heraus, dass die Analyse sich eignet zur Bestimmung von H_2S allein und (mit einer geringen Änderung) auch von SO_2 allein, aber nicht von beiden Verbindungen wenn sie gleichzeitig vorkommen.

Eine andere Analysenmethode, die neulich veröffentlicht wurde, hat diese Nachteile nicht.

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IMPEDANCE METHOD OF ZONE LOCALIZATION FOR PAPER CHROMATOGRAPHY WHICH OBVIATES THE NEED FOR PRELIMINARY SPRAYING

by

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In 1936 in connection with his work on conductimetric analysis and titration the writer showed that the difficulties due to polarization, adsorption, precipitation, cell cleaning, and electrode platinizing could be avoided by the employment of radio-frequencies which enable the electrodes to be separated from the solution and placed against the outside of a glass vessel containing the liquid. Since that date this device has come into general practice^{20,21}.

At first in 1936 the writer employed a heterodyne method for chemical analysis and measured variations in frequency caused by changes in solution concentration¹. He followed this in 1944-1945 with his Q-metric method again placing the electrodes on the outside of the glass tube which contained a sample of the solution¹⁻⁴.

In 1945 in conjunction with his rectified radio-frequency (R.Rf.) method of conductimetric analysis a similar tube fitted with external electrodes was employed⁴. This was followed in 1947 by his shielded "Conductimetric Tube"⁵⁻⁸.

CHROMATOGRAPHIC ZONE LOCATION

The method for locating chromatographic zones described in the present paper again makes use of the same principles.

When operating at a fixed frequency the impedance of the solution or substance which separates the electrodes is dependent upon conductance and dielectric constant.

When the conductance of the sample under test is high its dielectric constant will cause little or no appreciable effect. J. L. HALL and his associates^{9,10} when discussing the operation of cells having external electrodes also draw attention to the fact that the meter measurements are a function of the conductance and dielectric constants of the solution and state that whatever the type of cell its conductance will vary in accordance with the resistance of the solution.

Titration graphs when plotted are actually portions of a radio-frequency impedance curve relatively so large that for practical purposes the short portion covered is almost indistinguishable from a linear graph.

Conductance plays the major part in determining the meter deflections. The same remark applies also to those obtained for chromatographic zones as located by the writer's earlier methods^{11,12}, where the paper strips are sprayed with distilled water before localization.

CONSIDERATIONS

The filter paper used (on examination by the writer's moisture meter¹⁶) was found to be hygroscopic, and the idea occurred to him that matters might be arranged so that the chromatograph should make actual contact with the electrodes, and that under these conditions the zones might be sufficiently conductive after exposure to the air for a few hours. Were this to be so the necessity for spraying might be avoided^{11,12}.

It was also evident that the removal of the glass strips between which the chromatograph was sandwiched^{11,12} would reduce the impedance of the circuit.

EXPERIMENTAL TESTS

Fig. 1 shows the circuits and arrangement of the electrodes used for the first tests.

E and E' in this figure are two strips of metal foil which serve as electrodes, each is 16 cm long. They are attached to the adjacent edges of two sheets of glass (or better still polystyrene) G and G' separated by an air gap about 2 mm wide. The radio-frequency current from an oscillator* regulated by means of a small coupling condenser C (0.00001 μ F) is fed to electrode E. The second electrode E' is connected to earth through a germanium rectifier Re in the R.Rf. circuit. When only air bridged the gap between the electrodes only a minute rectified current was regis-

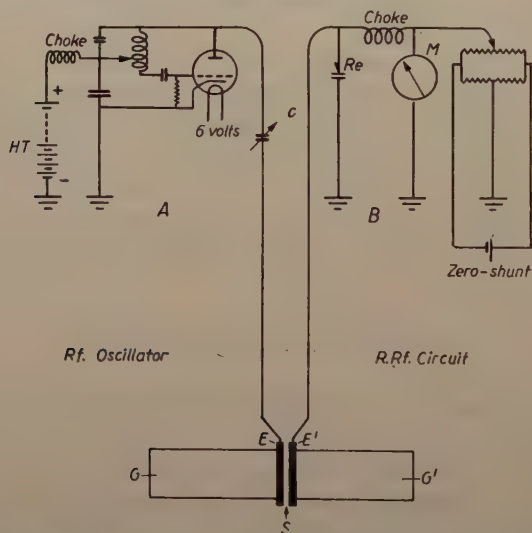


Fig. 1. A and B are circuit diagrams respectively of the oscillator and the rectifying circuits used in conjunction with BLAKE's "Doubled-electrode Zone Locator".

tered. The meter deflection was then set back to zero by the zero-shunt and an unsprayed chromatograph was passed slowly across the gap carefully keeping it in contact with the electrodes. A meter reading of 10 μ A was obtained for the filter paper between the zones, and very much larger readings for each zone according to its ionic concentration. These were quite comparable to the readings obtained for the same inorganic salts by the writer's original methods.

At this stage a difficulty was experienced — that of keeping the chromatograph evenly in contact with the electrodes as it was passed across the air gap S. Any uneven pressure or crinkling of the paper affected the meter readings. In the original methods^{11,12} sandwiching the paper between glass strips avoided this difficulty. With unsprayed paper however the use of glass was not practicable as its presence caused too great an increase in capacitance.

* Both the Hartley-Child oscillator and the R.Rf. circuits shown in the Figure are well known and have been described already¹³.

Doubled electrodes

Eventually a solution was found. The design and size of the electrodes was altered, and "doubled electrodes" were employed. The instrument as designed will take chromatographs of any width up to 14 cm.

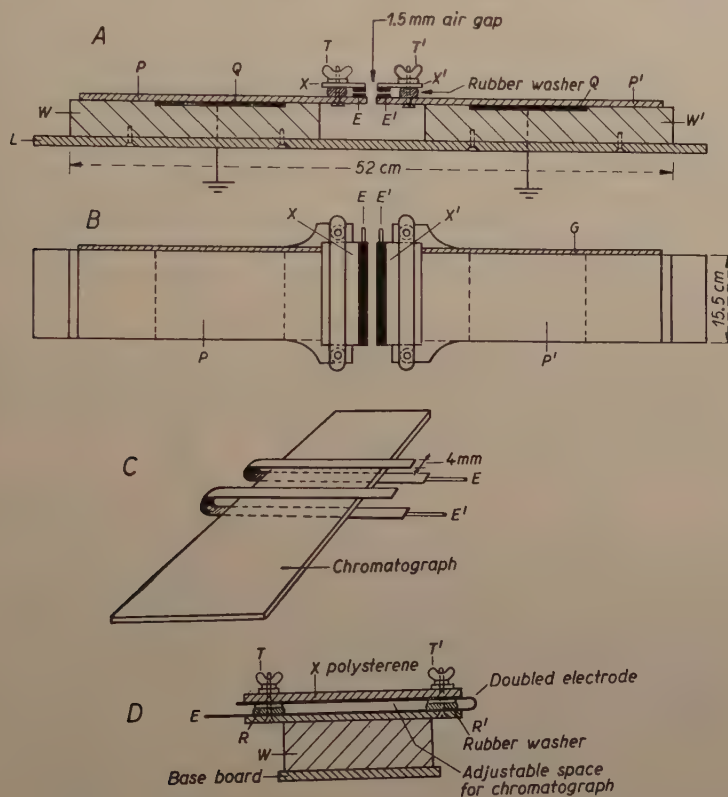


Fig. 2. A is a section of the Rf Zone Locator for conductive and non-conductive chromatographs. B shows the same instrument as viewed from above. C illustrates the passage of a chromatograph through the two "Doubled-electrodes" E and E'. D is the end view of the Zone Locator. In this diagram only one "Doubled-electrode" E is visible, the second electrode is behind it and out of sight.

Each of the two electrodes was formed by doubling over a strip of metal foil so that one half was exactly over the other as indicated in Fig. 2 C. During operation if no zone is present the space between the two halves of each electrode will always be occupied by the same total amount of air and paper (i.e., the dielectric constant will remain unchanged), therefore when the chromatograph is repeatedly passed across the gap between two such doubled electrodes the same deflections are obtained every time for each zone.

Doubled electrode R.Rf. chromatographic zone locator

The presence of a minute quantity of water picked up hygroscopically adds greatly to the conductivity of the chromatographs.

The construction of the zone locator is seen in Fig. 2 A which is a sectional sketch. Fig. 2 B shows the zone locator as viewed from above. P and P' are two sheets of 3 mm polystyrene each 15.5 cm wide except at their ends where the electrodes are attached, here they are widened sufficiently to allow for holes to be drilled to take the bolts and thumbscrews by means of which two strips of polystyrene X and X' are clamped in position. The upper halves of the electrodes E and E' are attached to the under surfaces of X and X', and their lower halves are fastened to the upper surface of P and P'.

The space between the surfaces of the electrodes (through which the chromatograph travels) is kept open by means of rubber washers and can be set to accord nicely with the thickness of the paper by four thumbscrews, only two of which T and T' are seen in the sketches. Fig. 2 D is a sectional end view showing X in position over the polystyrene sheet P.

As the thumbscrews T and T' are tightened the space between the upper and lower surfaces of the electrodes is gradually reduced.

It will be noted that the electrodes as mounted are supported well above the base L by wooden blocks W and W'.

Q and Q' are metal plates connected to earth; these restrict the field on either side of the electrodes, and prevent the proximity of the operator's hands from influencing the meter readings.

Screened circuits and leads

Both the oscillator and the rectifier circuits, Fig. 1 A and B, are earth screened, as also are the leads to the electrodes. The earthed screening is not shown in the figures.

A technique for recording the position and measurements of zone intensities

For this purpose a micro-ampere meter scale (corresponding to the scale on the micro-ammeter in the R.R.f. circuit) may be attached to the top of one of the "doubled electrodes" E., Fig. 2. Before the chromatograph is localized it is covered by a strip of thin paper (typewriting paper) and they are both passed together through the "doubled electrodes".

Recording

The meter deflections for each zone are read first and then recorded according to scale measurement on the paper which covers the chromatograph. The marking (a series of dots) is made with a pencil which is inserted through the gap between the upper halves of electrodes E and E', marking the cover paper where it lies across the gap. A general picture indicative of the variations in the impedance along the entire length of the chromatograph and the distribution of the zones is obtained by joining the ends of the recorded dots.

Sample chromatographs

Fig. 3 shows the plottings from a series of chromatographs. The gradual separation of CuCl_2 from KCl is seen over a period of five hours (solvent ethyl alcohol). On the actual chromatographs the shaded band was stained a light green by the CuCl_2 .

The KCl zone being colourless was not visible but it is clearly revealed by localization. The maxima and minima of ionic intensity are sharply defined. It is interesting to note that the original zone which contained both the CuCl_2 and the KCl before development are completely cleared of those substances as development progresses. After 5 hours the two zones are seen still to overlap, obviously a much longer time would be required for them to separate completely.

Circuits

The circuits shown in Fig. 1 were those employed and were amply sensitive. However where zones containing much smaller quantities, or less conductive substances are to be localized, up to sevenfold amplification can be obtained by employing the writer's "Dual purpose transistor circuit"¹⁴.

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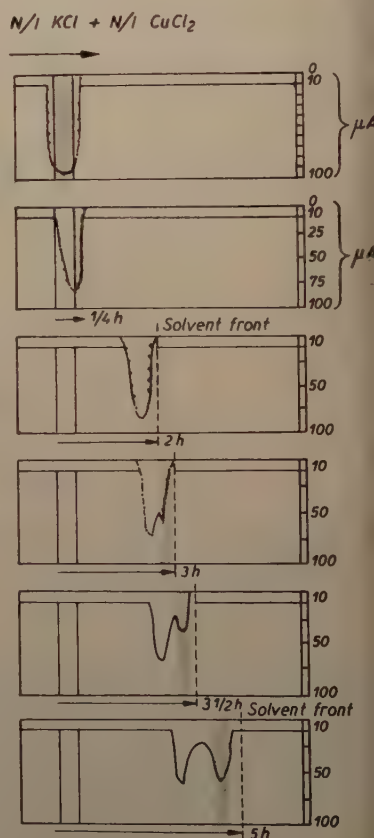


Fig. 3. In this figure the progress and separation of a mixture of the chlorides of copper and potassium is followed in a series of chromatographs over a period of five hours. The shaded band represents the faint green coloration of the CuCl_2 .

Technique

Gravity fed chromatographs. The method followed in developing and preparing the chromatographs Fig. 3 was as follows:

Six strips of No. 1 Whatman's filter paper each 10.5 cm wide and 25 cm long were tested for uniformity by passing them across the localizer. After this a band 2 cm wide was marked by two pencil lines 5 cm from one end of each, and equal quantities of 1 mol KCl and CuCl_2 (0.02 cm) were applied over each band thus marked out^{15,17}. They were then dried and suspended from a trough filled with a solvent of ethyl alcohol. The development took place in a closed developing chamber at the bottom of which (not touching the papers) there was a small quantity of equal parts of ethyl-alcohol and water, the evaporation from which kept the atmosphere saturated. As the temperature of the room was fairly constant no attempt was made to control it.

The container remained closed during the complete development of each chromatograph. When the desired time had elapsed the chromatograph was carefully dried and it was once more suspended over the ethyl-alcohol water mixture in the closed chamber and left there over night. In the morning it was ready to pass through the localizer.

For this test strong concentrations were employed in order that the green colour of the cupric chloride should be clearly visible.

Zone intensification

Experiment has shown that when only relatively weak solution concentrations are used for the chromatographs it is possible to intensify the zones temporarily by exposing them for twenty or thirty seconds to steam over a dish of boiling water. In this way the conductivity of the zones is greatly increased.

Dielectric comparisons

The following experiment was carried out with the simple arrangement of single electrodes already described in Fig. 1. This opens up the possibility of adapting the zone locator for the comparison of zones having dielectric (and semi-conductive) properties.

The experiment was as follows:

Samples of mica, rubber, paper of various thicknesses, and other materials some of which were partially conductive when placed across the electrodes each gave a distinctive meter deflection: It was of interest to note that the reading obtained for a small sample of window glass almost equalled that registered for a piece of metal of similar size separated from the electrodes by a sheet of dry paper.

NOTES AND SUGGESTIONS

As yet this work is in its early stages, doubtless many applications and variations in technique will be made. For example it may be possible to find some suitable substance with which to impregnate the paper before or after development in order to intensify the contrast between the conductance of the zones and the paper.

Up till now one of the difficulties encountered when distinguishing the solute contained in one zone from that in another zone has been the absence of any "exact mathematical point" or line¹⁸ in any zone from which Rf measurements^{17,18,19} could be made ($Rf = \frac{\text{Rate of solute travel}}{\text{Rate of solvent travel}}$).

The "Impedance" method of zone localization enables critical reference points to be located both for the regions of greatest density and for the edges of each zone. This method resembles the author's method for measuring the diffusion rate of liquids²². In both methods a region of given ionic density is selected as a point of reference which is then followed as it travels.

The following Rf values were obtained for metallic chlorides from "spot" chromatographs on No. 1 Whatman filter strips 2.5 cm wide (solvent *n*-butanol saturated with 3*N* HCl). After ascending development the chromatographs were hung up to

dry over night and the measurements were made the next morning by means of the "Doubled-electrode Zone Locator".

<i>Time of development</i>		<i>Rf Value</i>
Cu	1 h	0.210
	2 h	0.211
	3 h	0.215
Hg	3 h	0.813
A mixture of	3 h	Cu 0.222 and Hg 0.806
Cu and Hg	5 $\frac{1}{4}$ h	Cu 0.210 Hg 0.812

QUANTITATIVE ESTIMATIONS

With further reference to Fig. 3 the sharp definition of the areas containing the various solutes suggests the possibility of developing a technique for quantitative measurements.

Further work is proceeding with this object in view.

SUMMARY

In 1936, BLAKE suggested and then applied radio-frequency currents to chemical analysis. He demonstrated that when a Rf current pulses through a solution from which the electrodes are separated by an insulator the impedance of the circuit is comparable to that of a condenser bridged by a resistance. The author again makes use of such a circuit in his radio-frequency zone locator for paper chromatographs. Details of the circuits are given together with illustrative diagrams. A feature of this method is that the need for spraying the chromatographs is obviated. It is also suggested that a technique for quantitative measurement of the contents of each zone may be developed.

RÉSUMÉ

En 1936, BLAKE proposa l'application des courants de radio-fréquence à l'analyse chimique. Il démontra que lorsqu'un courant de radio-fréquence traverse une solution dans laquelle les électrodes sont séparées par un isolant, l'impédance du circuit peut être comparée à celle d'une capacité pontée par une résistance. L'auteur utilise un tel circuit pour détecter par radio-fréquence les zones des chromatogrammes sur papier. Les détails des circuits sont donnés, illustrés par des diagrammes. Cette méthode permet d'éviter de révéler les chromatogrammes. On se propose également de développer une technique d'analyse quantitative pour chaque zone.

ZUSAMMENFASSUNG

1936 schlug BLAKE die Anwendung der Radiofrequenz-Ströme für die chemische Analyse vor. Er zeigte, dass wenn ein Radiofrequenz-Strom durch eine Lösung geht, in welcher die Elektroden durch eine Isolation getrennt sind, die Impedanz des Stromkreises verglichen werden kann mit derjenigen, welche eine mit einem Widerstand verbrückte Kapazität aufweist. Der Autor verwendet einen solchen Stromkreis, um mit Radiofrequenz die Zonen der Papierchromatogramme aufzuzeigen. Die Einzelheiten der Stromkreise werden gegeben und durch Diagramme veranschaulicht. Diese Methode erlaubt die Entwicklung der Chromatogramme zu umgehen. Man beabsichtigt auch eine Technik zu entwickeln, welche die quantitative Analyse für jede Zone ermöglicht.

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PAPER CHROMATOGRAPHY OF FATTY ACIDS AND HALOGENATED ORGANIC ACIDS

by

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A paper chromatographic method is described for the separation and analysis of the volatile fatty acids and some halogenated organic acids. This was developed in order to identify certain acids formed in small quantities during the base-catalysed halogenation of aliphatic ketones¹.

EXPERIMENTAL

Apparatus and procedure

Whatman's No. 4 filter paper was used throughout, and the developing solvent contained 70% propanol and 30% concentrated ammonia². The quantity of acid on the paper should not exceed 50-100 μ g, as greater amounts give elongated spots on development, which makes it difficult to determine the R_F value accurately^{3,4}. A development time of about 18 hours was generally sufficient, the solvent reaching the bottom of the paper in about 20 hours.

Materials

Commercial samples of the acids were used whenever obtainable, and these were purified by conventional methods.

α -Bromo-propionic acid was prepared by direct bromination of propionic acid in presence of phosphorus trichloride and was purified by distillation under reduced pressure⁵.

With the exception of iodoacetic acid and β -iodo-propionic acid, of which commercial samples were available, the iodo-acids were prepared in small yield by refluxing the corresponding bromo-acids with potassium iodide in acetone⁶ and were purified by recrystallization from petroleum ether.

The acids were dissolved in dilute aqueous ammonia, and the resulting solutions of their ammonium salts were applied to the chromatograms.

Spraying reagents

The following reagents were used to locate the positions of the acids:

1. *Fatty acids.* The chromatograms were sprayed with a slightly alkaline solution of B.D.H. Universal Indicator (pH adjusted to 9.5)⁷; this avoids the necessity of maintaining a carbon dioxide-free atmosphere, which has to be used when thymol blue is the spraying reagent². Acids on the paper appeared as red spots on a blue background. The halogenated acids are also visible, but these can be distinguished from the unsubstituted acids by the procedures given below.

2. *Iodo-acids.* The developed chromatograms were allowed to hang for 5-10 seconds in a glass tank filled with dilute gaseous chlorine. The positions of the acids are visible as yellow spots on a white background. Chlorine liberates iodine from the iodo-acids, which reacts with ammonia (already present in the paper from the developing solvent) to give a "stain" due to formation of nitrogen iodides.

3. *Bromo-acids.* The chromatograms were sprayed with an 0.1% solution of fluorescein in 75% v/v aqueous ethanol, and the paper strips were then allowed to hang for about 5 seconds in a chlorine tank. The liberated bromine reacts with fluorescein on the paper and red spots, due to the formation of eosin, are visible on an almost white background, indicating the positions of the bromo-acids.

An 0.1% solution of α -naphthoflavone in acetone was also used as a spraying reagent, and the positions of the bromo-acids are then visible as orange-yellow spots. This reagent was not, however, as sensitive as fluorescein.

4. *Mixtures of bromo- and iodo-acids.* The chromatograms were sprayed with 0.1% fluorescein solution and were then allowed to hang for a few seconds in a chlorine tank. The bromo-acids are visible as red spots and the iodo-acids as intense yellow spots on an almost white background.

RESULTS

The method was standardized with solutions of some pure lower fatty acids and their bromo- and iodo-derivatives, and the R_F values of these acids are given in Table I. All results are average values for determinations carried out in triplicate;

TABLE I

R_F VALUES OF SOME LOWER FATTY ACIDS AND THEIR BROMO- AND IODO-DERIVATIVES

Acid	R_F value	Acid	R_F value	Acid	R_F value
HCOOH	0.38 (0.37)	CH ₂ .Br.COOH	0.45	CH ₂ I.COOH	0.50
CH ₃ .COOH	0.39 (0.37)	CH ₃ .CHBr.COOH	0.52	CH ₃ .CHI.COOH	0.55
CH ₃ .CH ₂ .COOH	0.48 (0.48)	CH ₂ Br.CH ₂ .COOH	0.52	CH ₂ I.CH ₂ .COOH	0.56
CH ₃ .CH ₂ .CH ₂ .COOH	0.57 (0.57)	CH ₃ .CH ₂ .CHBr.COOH	0.60	CH ₃ .CH ₂ .CHI.COOH	0.62
(CH ₃) ₂ .CH.COOH	0.57 (0.57)	(CH ₃) ₂ CBr.COOH	0.61	(CH ₃) ₂ CI.COOH	0.63
CH ₃ .CH ₂ .CH ₂ .CH ₂ .COOH	0.68 (0.69)	CH ₃ .(CH ₂) ₂ .CHBr.COOH	0.70	(CH ₃) ₂ CH.CHI.COOH	0.72
(CH ₃) ₃ C.COOH	0.70 (—)	(CH ₃) ₂ CH.CHBr.COOH	0.70		

The figures in brackets are the corresponding R_F values of the fatty acids determined by ISHERWOOD AND HANES⁶.

TABLE II

PAPER CHROMATOGRAPHIC SEPARATION OF MIXTURES OF LOWER FATTY ACIDS AND THEIR BROMO- AND IODO-DERIVATIVES

Components present	1st Component	R_F values 2nd Component	3rd Component
CH ₃ .COOH, CH ₂ I.COOH	0.39 (0.39)	0.50 (0.50)	—
CH ₃ .COOH, CH ₃ .CH ₂ .CH ₂ .COOH	0.39 (0.39)	0.56 (0.57)	—
CH ₂ Br.COOH, CH ₂ I.COOH	0.44 (0.45)	0.50 (0.50)	—
CH ₂ I.COOH, CH ₂ I.CH ₂ .COOH	0.49 (0.50)	0.55 (0.56)	—
CH ₂ I.COOH, CH ₃ .CH ₂ .CHBr.COOH	0.50 (0.50)	0.61 (0.60)	—
CH ₂ I.COOH, CH ₃ .CH ₂ .CH ₂ .COOH, CH ₃ .CH ₂ .CH ₂ .CHBr.COOH	0.50 (0.50)	0.55 (0.57)	0.69 (0.70)
CH ₃ .COOH, CH ₂ Br.COOH, CH ₃ .CH ₂ .CHBr.COOH	0.37 (0.39)	0.46 (0.45)	0.60 (0.60)
CH ₂ Br.COOH, CH ₂ I.COOH, CH ₃ .CH ₂ .CH ₂ .CHBr.COOH	0.45 (0.45)	0.51 (0.50)	0.69 (0.70)

The figures in brackets are the corresponding R_F values of the acids determined in blank runs (cf. Table I).

individual determinations varied from the mean value by not more than 2%. For the fatty acids, the R_F values are in good agreement with those found by ISHERWOOD AND HANES⁶.

In Table II are given some typical results obtained on chromatographic analysis of mixtures of fatty acids and halogenated organic acids, and it will be seen that the R_F values of all the compounds studied are unaffected by the presence of other components. In general, the R_F values appear to be largely a function of molecular weight, and isomeric compounds have the same R_F value.

ACKNOWLEDGEMENT

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SUMMARY

A paper chromatographic method is described for the identification of the volatile fatty acids and some of their bromo- and iodo-derivatives. Some new spraying reagents are suggested which enable the different classes of acids to be detected in presence of one another.

RÉSUMÉ

Une méthode chromatographique sur papier est décrite pour l'identification des acides gras volatils et quelques-uns de leurs bromo- et iodo-dérivés. Quelques réactifs révélateurs sont proposés pour permettre de déceler les différentes catégories d'acides en présence les uns des autres.

ZUSAMMENFASSUNG

Eine papierchromatographische Methode zur Identifizierung von flüchtigen Fettsäuren und einigen ihrer Brom- und Jodderivate wird beschrieben. Einige neue Entwicklungsreagenzien werden vorgeschlagen, die erlauben sollen, die verschiedenen Klassen von Säuren nebeneinander zu erkennen.

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A PRECISE, DIRECT, HETEROMETRIC MICRO-DETERMINATION OF
MERCURY WITH DIETHYLDITHIOCARBAMATE IN EXCESSES OF
METALS
ETHYLENEDIAMINETETRAACETATE SOLUTIONS

by

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INTRODUCTION

In a previous investigation¹ we showed that tenths of a mg of mercuric mercury or of diethyldithiocarbamic acid (CBM) in 20 ml solution, could be determined heterometrically with either CBM or mercuric nitrate, with an error of 0.2%. At room temperature the titration takes about half an hour.

In this paper further results are presented which were obtained in the presence of complexing agents, chiefly a strong ammoniated solution of ethylenediaminetetraacetate (= EDTA). The investigation was restricted to the use of dilute solutions of the latter and therefore the amount of foreign metal present was accordingly reduced. But as EDTA did not interfere with the main reaction, the amount of EDTA in the strong ammoniated solution could have been many times greater under these conditions. Consequently, the amount of the foreign metal which could be retained in solution, to give a complex with EDTA, could have been many times greater than that used in these experiments.

EXPERIMENTAL

The same apparatus and the same technique were used as in the previous heterometric investigation. 20 ml solution was used. The reaction vessel had a diameter of 4 cm. The titrations lasted ~30 minutes. Only in the case of copper, a green filter was tried but the results were not improved. Both the $\text{Na}_2\text{H}_2\text{EDTA}$ and the Na -diethyldithiocarbamate were pure and were Eastman products. The mercuric nitrate was a crystallised reagent $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ by Baker and Adamson.

The end-points were obtained from enlarged curves, by the intersection of the line of the last part of the titration curve with the horizontal maximum optical density line.

RESULTS

The composition and results of a selection of experiments are given in Table I. Selected experiments are presented in Figs. 1 and 2 (the same numeration is used in the table and in the figures).

In all cases, with the exception of copper, the first maximum optical density point was reached at the calculated end-point of the quantitative formation of $\text{Hg}(\text{CBM})_2$. In most cases the error was nearly zero, although in particular cases it was as high as 2.2%.

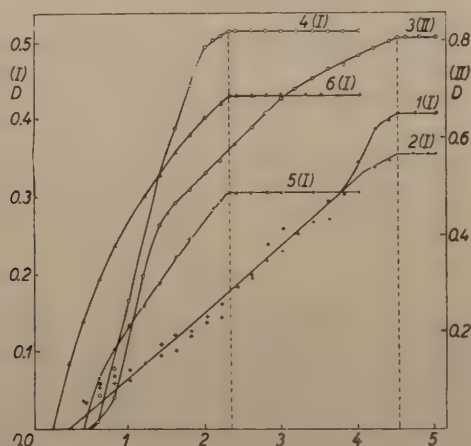


Fig. 1. The precipitation of mercuric carbamate in the presence of complexing agents.

Titration in the presence of complexing agents

Fig. 1 presents the results obtained in the presence of different complexing agents, but in the absence of foreign metals. In the presence of pyro- and tripolyphosphate (curves 1 and 2) disturbances occurred during the titrations, but the end-point was clear. Smooth titrations occurred in the presence of strong ammoniated citric acid (curve 6) or EDTA. In the presence of the latter, the maximum density values obtained were proportional to the amount of mercury which was titrated (curves 3-5). This is probably due to the gradual precipitation of mercury which formed a complex with EDTA and to the formation of final uniform particles of $\text{Hg}(\text{CBM})_2$. It is interesting to note that in curve 3, Fig. 1 intermediate breaks may be discerned in addition to the final compound of $\text{Hg}(\text{CBM})_2$.

Titration in the presence of foreign metals

Table I shows the composition of the experiments and the results obtained. In all cases the molar ratios of mercury to the foreign metal were either 1 : 17 or 1 : 33. In no case did the presence of the foreign metal appreciably change the maximum optical density value as compared to the blank. In the case of copper alone, no constant maximum density line was reached and the densities increased continuously. In the presence of silver no precipitation occurred. With chromium a precipitation appeared before the beginning of the titration.

TABLE I

General composition: 3 ml $\text{Hg}(\text{NO}_3)_2$ aM + K ml supplements + (17- K) ml H_2O + x ml diethyldithiocarbamate (= CBM) bM. Temp. 20°

Expt. nos.	Solution			Molarity of $\text{Hg}(\text{NO}_3)_2$ (a)	Found CBM x ml	Maxim. density value	Initial precip. at ml	Titration time (min)	Theoretical at ml	% error
1	1 ml	$\text{Na}_4\text{P}_2\text{O}_7$	0.125M	0.002	0.0028	4.45	0.41	60	4.5	-1.1
2	1 "	$\text{Na}_6\text{P}_3\text{O}_{10}$	0.2 "	0.002	0.0028	4.50	0.36	40	4.5	0.0
3	4 "	$\text{Na}_2\text{H}_2\text{EDTA}$	0.05M	0.002	0.0028	4.45	0.80	30	4.5	-1.1
4	4 "	"	"	0.001	0.0028	2.30	0.52	40	2.25	+2.2
5	4 "	"	"	0.0005	0.0014	2.30	0.30	45	2.25	+2.2
6	1 "	$\text{Na}_3\text{-citrate}$	M	0.001	0.0028	2.25	0.43	25	2.25	0.0
7	2 "	Na-acetate	0.1M	0.002	0.0028	4.50	0.70	15	4.5	0.0
8	1 "	CH_3COOH	M	0.002	0.0028	4.45	0.85	30	4.5	-1.1
9	1 "	"	"	0.0005	0.0014	2.25	0.29	20	2.25	0.0
10	4 "	$\text{Na}_2\text{H}_2\text{EDTA}$	0.05M	0.002	0.0028	4.45	0.80	30	4.5	-1.1
11	4 "	"	"	0.001	0.0028	2.25	0.53	35	2.25	0.0
12	4 "	"	"	0.0005	0.0014	2.18	0.27	35	2.25	0.0
13	4 "	"	"	0.001	0.0028	2.25	∞	40	2.25	0.0
14	4 "	"	"	0.001	0.0028	2.25	0.51	40	2.25	0.0
15	4 "	"	"	0.001	0.0028	2.25	0.49	40	2.25	0.0
16	4 "	"	"	0.001	0.0028	2.25	0.52	35	2.25	0.0
17	4 "	"	"	0.001	0.0028	2.25	0.52	35	2.25	0.0
18	4 "	"	"	0.001	0.0028	2.30	0.50	30	2.25	+2.2
19	4 "	"	"	0.001	0.0028	2.30	0.51	30	2.25	+2.2
20	4 "	"	"	0.001	0.0028	2.30	0.54	30	2.25	+2.2
21	4 "	"	"	0.001	0.0028	2.30	0.57	40	2.25	+2.2
22	4 "	"	"	0.001	0.0028	2.25	0.57	45	2.25	0.0
23	4 "	"	"	0.001	0.0028	2.25	0.52	35	2.25	0.0
24	4 "	"	"	0.001	0.0028	2.25	0.47	35	2.25	0.0
25	4 "	"	"	0.001	0.0028	2.30	0.57	45	2.25	+2.2

Experiments 7 and 8 (Table I) are interesting, since in the former case the initial precipitation occurs at the molar ratio of 1 Hg : 0.7 CBM and in the latter the precipitation began at the ratio 1 Hg : 1.4 CBM. This difference in behaviour is caused by the different pH's at which the titration is made.

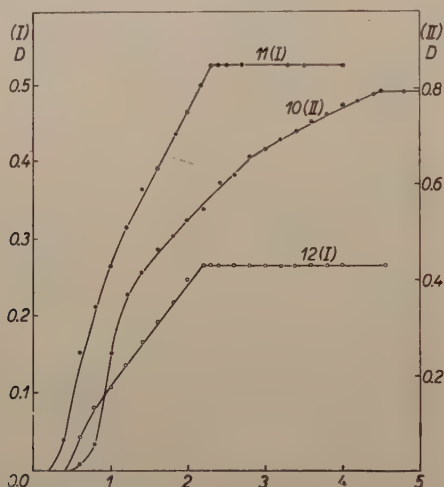


Fig. 2. The precipitation of mercury in the presence of bismuth.

Fig. 2 shows the course of the titrations in the presence of bismuth (molar ratios 1 : 17 to 1 : 66). In these experiments the maximum values obtained were approximately proportional to the amount of mercury analysed (0.3 mg — 1.2 mg Hg).

CONCLUSIONS

On the basis of the experiments presented in this paper, we conclude that *a solution of EDTA containing excesses of ammonia retains all the alien metals (with the exception of copper) as complexes and that the titration of minute amounts of mercury with NaCBM can be carried out smoothly without any interference.*

The percentage of mercury may be very low, e.g. in the case of bismuth, it may be 1% or less.

METHOD

20 ml aqueous solution which contains 0.3-1.2 mg mercuric mercury and any quantity of bivalent metals or polyvalent iron, (aluminium), bismuth or thorium, is analysed directly by heterometric titrations with 0.0028M sodium diethyldithiocarbamate.

The solution must contain an excess of ethylenediaminetetraacetate and a corresponding excess of ammonia in order to obtain a high pH. The titration time is 30-40 minutes and the error is 0.2%.

SUMMARY

0.3-1.2 mg mercury in 20 ml aqueous solution is analysed with sodium diethyldithiocarbamate. The solution may contain any amount of other bivalent metal or iron (III), bismuth or thorium. A corresponding excess of ethylenediaminetetraacetate and ammonia must then be added. The error is 0-2%.

RÉSUMÉ

0.3 à 1.2 mg de mercure dans 20 ml de solution aqueuse peuvent être dosés au moyen de diéthyl-dithiocarbamate de sodium. Ce dosage peut être effectué en présence d'autres cations bivalents et en présence de fer (III), de bismuth et de thorium. Un excès correspondant d'éthylènediamine-tétraacétate et d'ammoniaque doit alors être ajouté. L'erreur est comprise entre 0 et 2%.

ZUSAMMENFASSUNG

0.3-1.2 mg Quecksilber in 20 ml wässriger Lösung werden mit Natriumdiäthyl-dithiocarbamat analysiert. Die Lösung kann beliebige Mengen anderer zweiwertiger Metalle sowie Eisen (III), Wismuth oder Thorium enthalten. Ein entsprechender Überschuss an Äthylendiamintetraacetat und Ammoniak muss dann hinzugefügt werden. Fehler: 0-2%.

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THE AURINTRICARBOXYLATES OF ALUMINIUM, IRON AND CHROMIUM

COMPOSITION, STRUCTURE AND ANALYTICAL USE A HETEROMETRIC STUDY

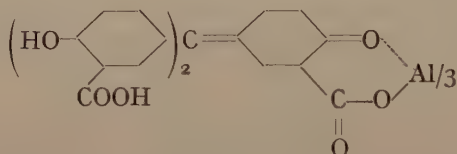
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INTRODUCTION

Ammonium aurintricarboxylate (aluminon = AN) is used extensively for the detection of aluminium and for the quantitative determination of aluminium, beryllium *etc.*¹ The composition of the compounds which are obtained at different pH's have not been thoroughly investigated. In the case of aluminium, the compound obtained from slightly acid solution is generally presented as:



The analytical aspect of the problem is connected with the colour intensity and the stability of the compounds obtained at different pH's. An intense red solution is obtained and the intensity of the colour is measured. The presence of iron or chromium interferes with the results obtained in an analysis of an aluminium solution. The hypothesis generally accepted is that the AN forms "lakes" with the cations. The study of the character and the composition of the „lakes" involves great difficulties as no methods exist for their study. As the study of chemical reactions in suspensions is of special concern to us, we were interested in investigating the reactions with AN and in seeing to what extent they proceed stoichiometrically, and if and when precipitation occurs.

Our study was limited to the trivalent cations. Preliminary heterometric titrations with other bi- and polyvalent cations were carried out in order to obtain a general picture of the reaction of cations with AN. From our experiments it could be deduced that all the trivalent cations form a series of well defined compounds with AN. These were formed successively from one another on the addition of AN to the cation or vice versa. The existence of both intermediates and final compounds was esta-

lished. The heterometric titrations were completed in a short time and the reactions studied proceeded smoothly and stoichiometrically.

The compounds of iron were much more stable than those of aluminium or chromium. Even in a solution with a molar ratio of 100 Al:1 Fe the iron compounds were formed first and quantitatively.

The analytical aspect of the investigation was studied separately.

EXPERIMENTAL

The same apparatus and the same working conditions were observed as in previous heterometric investigations²⁻³. The temperature of the reaction vessel was thermostatically controlled during the titration. All titrations were carried out at 20° C. The reaction vessel had a diameter of 4 cm.

The reagents used were all c.p. or analytical reagents. No difference in the results was observed whether the trivalent salts were chlorides or nitrates. In order to avoid hydrolysis, all dilute solutions of iron were prepared from an iron nitrate stock solution (0.1M) which contained added free nitric acid in a molar concentration twice as high as the molarity of the iron nitrate (e.g. a 0.005M $\text{Fe}(\text{NO}_3)_3$ solution was 0.01M in HNO_3). The highly diluted solutions of iron nitrate were nevertheless freshly prepared from the more concentrated stock solutions. The AN used was a BDH c.p. reagent.

The isolation of the solid compounds

A deep red Corning filter (No. 2408) was used throughout this investigation. This was done in order to eliminate, as far as possible, the colour effect of AN during the titration and to measure the density caused by the formation of the precipitation only. It cannot be said with certainty to what extent this goal was achieved as we were working in a complicated sol-gel system. The clear breaks at the critical end-points in the curves presented prove that the guiding principles held in all cases, and the breaks obtained corresponded to the quantitative formation of solid compounds of definite composition.

Reaction time

Generally in the more important titrations the time necessary for a full titration was between ten and twenty minutes. But in special cases when additional information was of interest, the titration time was extended somewhat. This indicates that the reactions studied are of a relatively simple nature. No complications whatsoever were caused by the physical state of the precipitates as compared with other precipitates which have been studied heterometrically.

RESULTS AND DISCUSSION

A. The reaction between aluminium and AN

pH-Heterometric titrations

Fig. 1 presents the composition and results of heterometric titrations which were carried out by the dropwise addition of nitric acid to solutions containing a buffer mixture in addition to aluminium and AN. Curve 4 shows a parallel blank pH-titration carried out with the buffer mixture. The pH's of expts. 1-3 can be taken from this curve. The heterometric titrations were carried out in solutions of a molar ratio 1 Al : 1 AN (curve 1), 1 Al : 2 AN (curve 2) and 1 Al : 3 AN (curve 3). No other molar ratios were ever found at the critical points of the heterometric titrations. Analysing the curves of Fig. 1. the following may be deduced: no precipitation occurred at high pH's in any experiment. In expt. 1. (1 Al : 1 AN) the precipitation practically began at pH \sim 8 and was completed at pH \sim 4. The precipitate was of bright red color. At lower pH's the precipitate very slowly dissolved. The results of expts. 2 (1 Al : 2 AN) and 3 (1 Al : 3 AN) are more definite and clearer. In both cases the precipitation began at pH \sim 6 and was completed at pH \sim 3. Whilst in

expt. 2 some decrease in the densities occurred at $\text{pH} < 2$, no influence whatever was noticeable in expt. 3. The character of the lower parts of curves 2 and especially 3, indicates that in the pH region of 4-6 the course of the precipitation is somewhat different than in the pH region of 3-4. Summarizing, it may be said that aluminium may be precipitated either as $\text{Al}(\text{AN})_2$ or $\text{Al}(\text{AN})_3$ at pH's $\sim 3 \sim 4$.

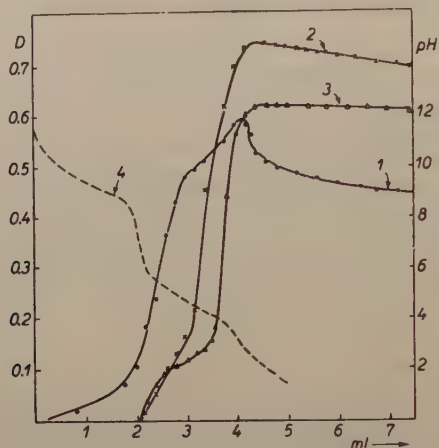


Fig. 1

1. 3 ml 0.02M AlCl_3 + 3 ml 0.02M Aluminon + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4.5 ml M NaOH + 5.5 ml H_2O + x ml M HNO_3 .
2. 2 ml 0.02M AlCl_3 + 4 ml 0.02M Aluminon + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4.5 ml M NaOH + 5.5 ml H_2O + x ml M HNO_3 .
3. 2 ml 0.02M AlCl_3 + 6 ml 0.02M Aluminon + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4.5 ml M NaOH + 3.4 ml H_2O + x ml M HNO_3 .
4. pH curve blank. Titration time, 15-30 minutes.

Titration of aluminium with AN

Fig. 2 presents a selection of results obtained with AlCl_3 or $\text{Al}(\text{NO}_3)_3$ in the presence or in the absence of excesses of acetic acid. In all cases the *first* maximum optical density point was obtained exactly at the calculated point of the quantitative formation of $\text{Al}(\text{AN})_3 \downarrow \downarrow$. No other intermediates were obtained. The values of the maximum density in curves 1 and 2 were almost proportional to the concentration of aluminium. In acetic acid solutions (curves 3 and 4) lower values were obtained.

Titration of AN with aluminium

Fig. 3 presents the composition and the results of some experiments. When AN was titrated with Al, the first maximum optical density was obtained, in all curves, exactly at the calculated point on the abscissa for the quantitative formation of $\text{Al}(\text{AN})_2 \downarrow \downarrow$. On further addition of aluminium, a horizontal density line was obtained, indicating that the compound is final. In curves 2 and 4, the existence of a more soluble compound of the composition $\text{Al}(\text{AN})_3$ could be traced, but this compound was then transformed into $\text{Al}(\text{AN})_2 \downarrow \downarrow$. In these titrations no proportionality seemed to exist between the values of the maximum density and the amount of AN which was titrated.

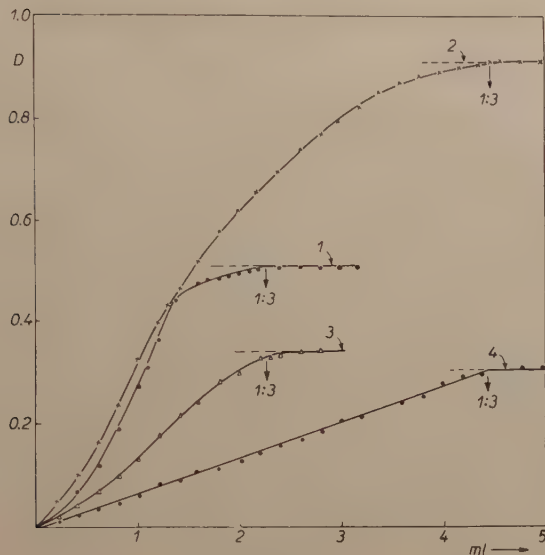


Fig. 2

1. 3 ml 0.005M AlCl_3 + 7 ml H_2O + x ml 0.02M Aluminon.
 2. 3 ml 0.01M AlCl_3 + 7 ml H_2O + x ml 0.02M Aluminon.
 3. 3 ml 0.005M $\text{Al}(\text{NO}_3)_3$ + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.02M Aluminon.
 4. 3 ml 0.005M $\text{Al}(\text{NO}_3)_3$ + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.01M Aluminon.
- Titration time, 20 minutes. Red filter.

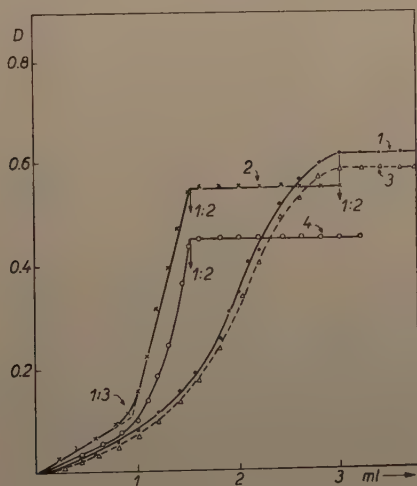


Fig. 3

1. 3 ml 0.02M Aluminon + 7 ml H_2O + x ml 0.01M AlCl_3 .
 2. 3 ml 0.01M Aluminon + 7 ml H_2O + x ml 0.01M AlCl_3 .
 3. 3 ml 0.02M Aluminon + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.01M $\text{Al}(\text{NO}_3)_3$.
 4. 3 ml 0.01M Aluminon + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.01M $\text{Al}(\text{NO}_3)_3$.
- Titration time, 20 minutes. Red filter.

B. The reaction between iron and AN

pH-Heterometric titrations

The titrations were similar to the pH-heterometric titrations with aluminium. The composition of the experiments and the results obtained are seen in Fig. 4. The molar ratios chosen were the same as with aluminium:

1 Fe : 1 AN (curve 5), 1 Fe : 2 AN (curve 4) and 1 Fe : 3 AN (curves 2 and 3). The blank pH curve is presented in curve 1. In no case did a precipitation occur at pH > 9. In all cases the precipitation began at pH \sim 8. The main precipitation occurred at pH 6-4. Below pH \sim 4 the precipitate gradually redissolved. The precipitate was of violet colour. The pH-region of precipitation is therefore between 8 and 4. In the case of iron the decisive role is probably played by the compound $\text{Fe}^{\text{III}}_1(\text{AN})_1$ and therefore the curves 3-5 are of the same character.

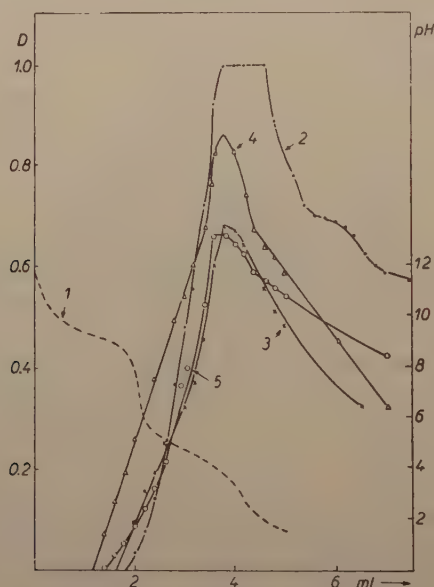


Fig. 4

1. pH blank curve.
 2. 2 ml 0.005M $\text{Fe}(\text{NO}_3)_3$ + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4 ml M NaOH + 6 ml 0.005M Aluminon + 4 ml H_2O + x ml M HNO_3 .
 3. 2 ml 0.0025M $\text{Fe}(\text{NO}_3)_3$ + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4 ml M NaOH + 6 ml 0.0025M Aluminon + 4 ml H_2O + x ml M HNO_3 .
 4. 2 ml 0.005M $\text{Fe}(\text{NO}_3)_3$ + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4 ml M NaOH + 4 ml 0.005M Aluminon + 6 ml H_2O + x ml M HNO_3 .
 5. 2 ml 0.01M $\text{Fe}(\text{NO}_3)_3$ + 2 ml M CH_3COOH + 2 ml M NH_4NO_3 + 4 ml M NaOH + 2 ml 0.01M Aluminon + 8 ml H_2O + x ml M HNO_3 .
- Titration time, 10 minutes. Red filter.

Titration of iron with AN

Fig. 5 presents the composition and results of titrations carried out in the absence of acetic acid. The same amount of iron was titrated with AN of different concentrations. Fig. 6 shows similar titrations but in the presence of excesses of acetic

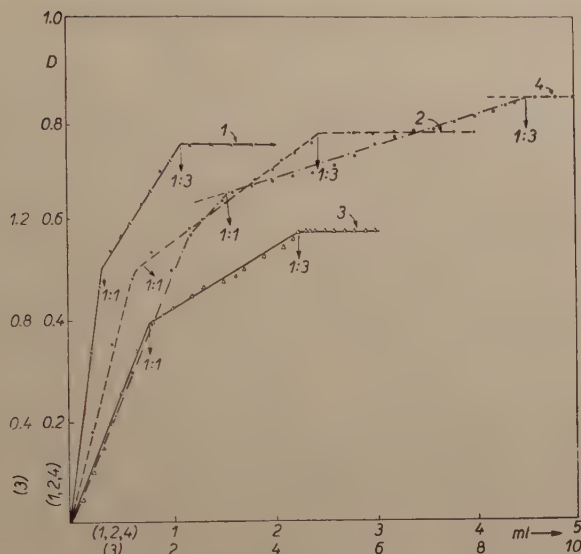


Fig. 5

1. 3 ml 0.0025M $\text{Fe}(\text{NO}_3)_3$ + 7 ml H_2O + x ml 0.02M Aluminon.
 2. 3 ml 0.0025M $\text{Fe}(\text{NO}_3)_3$ + 7 ml H_2O + x ml 0.01M Aluminon.
 3. 3 ml 0.0025M $\text{Fe}(\text{NO}_3)_3$ + 7 ml H_2O + x ml 0.005M Aluminon.
- Titration time, 20 minutes. Red filter.

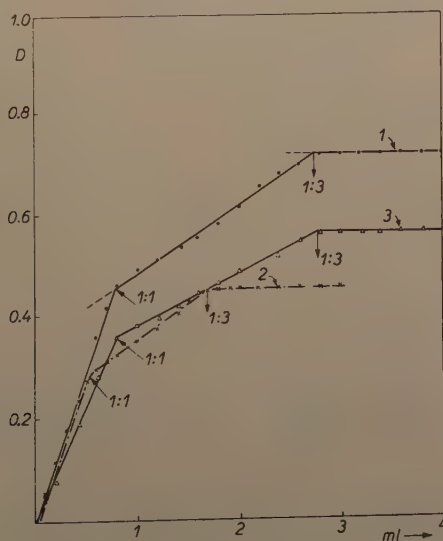


Fig. 6

1. 5 ml 0.00125M $\text{Fe}(\text{NO}_3)_3$ + 1 ml M CH_3COOH + 4 ml H_2O + x ml 0.0066M Aluminon.
 2. 3 ml 0.00125M $\text{Fe}(\text{NO}_3)_3$ + 1 ml M CH_3COOH + 6 ml H_2O + x ml 0.0066M Aluminon.
 3. 5 ml 0.00125M $\text{Fe}(\text{NO}_3)_3$ + 1 ml 0.1M HNO_3 + 4 ml H_2O + x ml 0.0066M Aluminon.
- Titration time, 10-15 minutes. Red filter.

acid (curves 1 and 2) or in the presence of nitric acid (curve 3). In all cases in Fig. 5 precipitation occurred immediately with the addition of the first drop of AN, showing that the compound obtained was very insoluble. In all cases the densities rose steeply and linearly to the first break which was obtained at the molar ratio of 1 Fe : 1 AN. $\text{Fe}_1(\text{AN})_1$ was precipitated quantitatively. On further addition of AN the density again rose linearly but the density line took another direction. A second break was obtained in all cases exactly at the molar ratio of 1 Fe : 3 AN $\downarrow\downarrow$. On further addition of AN a horizontal density line was then obtained. Excesses of AN had no influence on the final compound. In this case also, the titrations lasted 10-20 minutes. The course of the titration, as well as the densities which were obtained, did not change noticeably on varying the concentration of AN. The above breaks in each curve can also be utilized for an exact and rapid determination of iron(III).

As far as the influence of acids on the results (Fig. 6) are concerned, the following may be said: with the same amount of iron used for the titration, the density values at the breaks are of the same order of magnitude with or without acetic acid. The density values obtained (curves 1 and 2) are proportional to the amount of iron in solution. The character of the curves of Figs. 5 and 6 indicates that the precipitate is very regular, probably giving particles of the same size. The presence of excesses of a strong acid (HNO_3) seems to depress the density values obtained (curve 3).

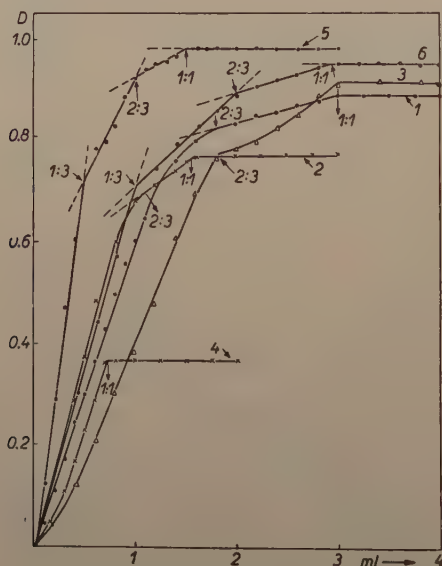


Fig. 7

1. 3 ml 0.01M Aluminon + 7 ml H_2O + x ml 0.01M $\text{Fe}(\text{NO}_3)_3$
2. 3 ml 0.005M Aluminon + 7 ml H_2O + x ml 0.01M $\text{Fe}(\text{NO}_3)_3$
3. 3 ml 0.005M Aluminon + 7 ml H_2O + x ml 0.01M $\text{Fe}(\text{NO}_3)_3$
4. 2 ml 0.002M Aluminon + 8 ml H_2O + x ml 0.005M $\text{Fe}(\text{NO}_3)_3$
5. 3 ml 0.005M Aluminon + 1 ml 0.1M CH_3COOH + 6 ml H_2O + x ml 0.01M $\text{Fe}(\text{NO}_3)_3$
6. 3 ml 0.005M Aluminon + 1 ml 0.1M CH_3COOH + 6 ml H_2O + x ml 0.005M $\text{Fe}(\text{NO}_3)_3$

Titration time, 10 minutes. Red filter.

C. Reaction between chromium(III) and AN

pH-Heterometric titrations

Buffer mixtures, were used, similar to those used in the case of aluminium (or iron), but as the chromium was less sensitive to AN than the other metals, the mixtures contained higher concentrations of AN (*cf.* Fig. 8).

In the presence of a buffer mixture identical to that used previously, a brown precipitate was obtained even before the addition of nitric acid. An acid buffer mixture was therefore tried instead (composition: 2 ml NH_4NO_3 M + 2 ml CH_3COOH M + 1 ml HNO_3 M) with the intention of titrating with NaOH, but unfortunately a red precipitate appeared even before the addition of the base. We were therefore compelled to give up the idea of such titrations.

Titration of chromium with AN

Fig. 8 shows the composition and results of titrations of chromium with AN. Only curve 1 shows breaks at 1 Cr : 1 AN and possibly 1 Cr : 2 AN. On titrating with a more highly concentrated AN-solution, no clear breaks were obtained.

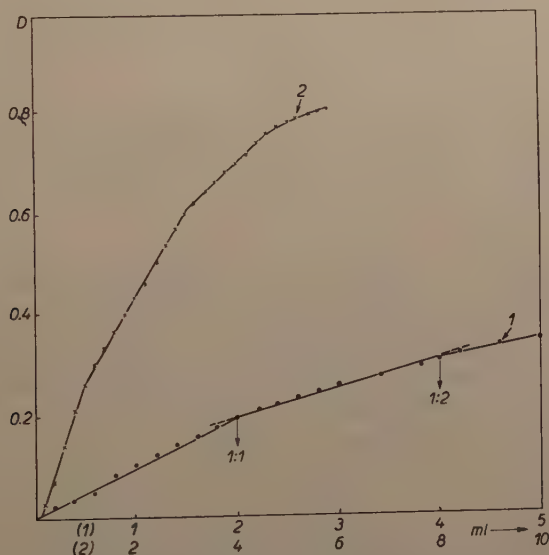


Fig. 8

1. 4 ml 0.005M $\text{Cr}(\text{NO}_3)_3$ + 6 ml H_2O + x ml 0.01M Aluminon.
2. 4 ml 0.01M $\text{Cr}(\text{NO}_3)_3$ + 6 ml H_2O + x ml 0.02M Aluminon.

Titration time, 15 minutes. Red filter.

Titration of AN with chromium

In contrast to the results shown in Fig. 8 clear breaks were obtained in the reverse titrations of AN with $\text{Cr}(\text{NO}_3)_3$ (Fig. 9). Curves 1-3 show results of titrations carried out in the absence of acetic acid. Curve 4 gives the results of a titration of identical composition to that of curve 3, but containing, in addition, acetic acid. The sensitivity of the chromium towards acetic acid is surprising: the densities obtained in the presence of acetic acid are almost one third as high as those obtained in its absence.

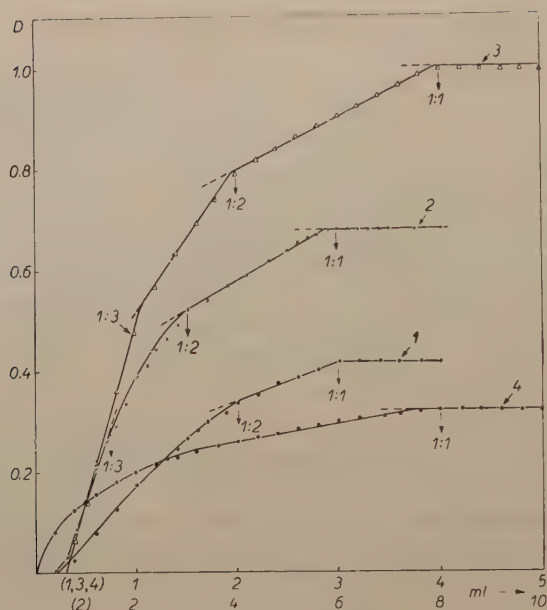


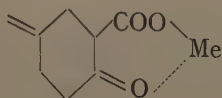
Fig. 9

1. 3 ml 0.01M Aluminon + 7 ml H₂O + x ml 0.01M Cr(NO₃)₃.
 2. 6 ml 0.01M Aluminon + 4 ml H₂O + x ml 0.01M Cr(NO₃)₃.
 3. 4 ml 0.02M Aluminon + 6 ml H₂O + x ml 0.02M Cr(NO₃)₃.
 4. 4 ml 0.02M Aluminon + 1 ml M CH₃COOH + 5 ml H₂O + x ml 0.02M Cr(NO₃)₃.
- Titration time, 20 minutes. Red filter.

In all four experiments the final break was obtained exactly at the molar ratio of 1 Cr : 1 AN (= CrAN). A further addition of Cr had no influence whatever on the compound CrAN and a horizontal density line was obtained in all cases. Intermediate clear breaks were obtained in the curves 1-3 at the molar ratio of 1 Cr : 2 AN (= Cr(AN)₂). A clear break at the ratio 1 Cr : 3 AN (Cr(AN)₃) was detectable only in curve 3. In curve 4 these breaks were blurred.

DISCUSSION

The results of this investigation show that AN gives precipitates of a definite composition with all three cations. In all cases, stoichiometric reactions occur. The optimum pH at which these precipitations occur is pH \sim 4. In the case of iron, precipitation occurs at pH 7-8 and with chromium the precipitate is formed at even higher pH's. In contrast to these, aluminium forms detectable precipitates with AN only in acid solutions at pH 4-6. It is difficult to describe with certainty the character of the compounds which are formed in alkaline solutions. They may be neutralized oxycomplexes which are formed in solution and which have the group:



Thus, during the study of the pH condition of the formation of the precipitates, a picture was obtained of the pH conditions which were necessary to hold the compounds "dissolved".

From the working conditions at 20° C it could be seen that 10-20 minutes were sufficient to obtain a detailed heterometric curve with all its breaks (= critical points). It can therefore be concluded that both the intermediate and the final reactions proceed smoothly and are not affected by the physical nature of the precipitates. It is remarkable how easily an intermediate *insoluble* compound is transformed quantitatively on the addition of either AN or Me^{+3} , into another insoluble compound.

With regard to the composition of the final insoluble compounds which were obtained on the addition of Me^{+3} to AN, in the case of iron or chromium they were composed as $Me^{III}_1(AN)_1 \downarrow\downarrow$ whilst in the case of aluminium $Al(AN)_2$ was obtained. It is surprising that $Al_1(AN)_1$ does not exist as an insoluble compound. On the other hand, in the case of iron an insoluble compound $Fe(AN)_2$ was never detected. In the case of chromium only the titrations in which Cr was added to AN gave clear-cut results: insoluble compounds of the composition $Cr(AN)_2 \downarrow$ and $Cr_1(AN)_1 \downarrow\downarrow$ were formed. $Cr(AN)_3$ could only be detected in certain experiments.

The composition of the insoluble compounds obtained with chromium were partly analogous to aluminium (= $Me^{III}(AN)_2$) and partly analogous to iron (= $Me^{III}_1(AN)_1$).

The different reactions which are of an ionic character are presented below, without consideration of the charges of the ionic components.

I. a $Me^{+3} + x AN$:

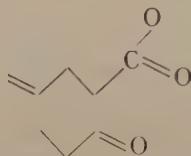
1. $Al + 3 AN \rightarrow \overline{Al(AN)_3} \downarrow\downarrow$
2. $Fe + AN \rightarrow \overline{Fe_1(AN)_1} \downarrow$
3. $Fe_1(AN)_1 + 2 \overline{AN} \rightarrow \overline{Fe(AN)_3} \downarrow\downarrow$
4. $(Cr + AN \rightarrow \overline{Cr_1(AN)_1} \downarrow)$

II. a $AN + x Me^{+3}$:

5. $(3 AN + Al \rightarrow \overline{Al(AN)_3} \downarrow)$
6. $(2 \overline{Al(AN)_3} + Al \rightarrow 3 \overline{Al(AN)_2} \downarrow\downarrow)$
7. $2 AN + Al \rightarrow \overline{Al(AN)_2} \downarrow\downarrow$
8. $(3 AN + Fe \rightarrow \overline{Fe(AN)_3} \downarrow?)$
9. $(\overline{Fe(AN)_3} + Fe \rightarrow \overline{Fe_2(AN)_3} \downarrow)$
10. $3 AN + 2 Fe \rightarrow \overline{Fe_2(AN)_3} \downarrow$
11. $\overline{Fe_2(AN)_3} + Fe \rightarrow 3 \overline{Fe_1(AN)_1} \downarrow\downarrow$
12. $3 AN + Cr \rightarrow \overline{Cr(AN)_3} \downarrow$
13. $2 \overline{Cr(AN)_3} + Cr \rightarrow 3 \overline{Cr(AN)_2} \downarrow$
14. $2 AN + Cr \rightarrow \overline{Cr(AN)_2} \downarrow$
15. $\overline{Cr(AN)_2} + Cr \rightarrow 2 \overline{Cr_1(AN)_1} \downarrow\downarrow$

(The compounds underlined are those corresponding to the clear breaks in heterometric curves.) Of the different compounds obtained those of iron are probably the most stable. When the mixtures, which contain traces of iron, and both chromium and aluminium in large excesses, were titrated with AN, the reaction proceeded quantitatively with iron alone at first.

The remarkable fact must be established that in our investigation on AN we never met with compounds which contained *more than one* mol cation per *one* mol AN. We may see the reason for this in the electronic structure of the chinoide formula which prevents the other salicylate-groups from functioning freely. It must therefore be assumed that of the *three* pairs of carboxylic and hydroxy-groups merely *one* pair can function in the complex formation. This group is probably as follows:



SUMMARY

1. With all three cations, insoluble, well-defined compounds were obtained. These are formed successively one from another.
2. The reactions proceeded smoothly and stoichiometrically, giving compounds of the molar ratios of cation to aluminon: 1:1, 1:2, and 1:3.
3. The pH-heterometric conditions of the precipitation were studied in each case.
4. Formulas for the single reactions are given in the paper.
5. The analytical aspect of the determination of traces of iron in the presence of excesses of aluminium and chromium, was emphasized in the investigation.

RÉSUMÉ

1. Des composés insolubles et bien définis ont été obtenus avec les trois cations étudiés. Ils se forment successivement, l'un provenant de l'autre.
2. Les réactions s'effectuent régulièrement et stoechiométriquement, dans les rapports moléculaires cation/aluminon suivants: 1:1, 1:2 et 1:3.
3. Les conditions de pH de précipitation ont été étudiées dans chaque cas.
4. Les équations des réactions sont données.
5. Le côté analytique du dosage des traces de fer, en présence d'excès d'aluminium et de chrome, a été particulièrement développé.

ZUSAMMENFASSUNG

1. Genau definierte Verbindungen wurden mit allen drei Kationen erhalten. Diese Verbindungen entstehen sukzessive aus einander.
2. Die Reaktionen verlaufen glatt und stöchiometrisch. Verbindungen von molarem Verhältnis von Kation zu Aluminon gleich 1:1, 1:2 und 1:3 wurden erhalten.
3. Die pH-heterometrischen Bedingungen der Fällung wurden in jedem einzelnen Fall studiert.
4. Die Formulierung der einzelnen Reaktionen wird in der Arbeit dargestellt.
5. Die Möglichkeit der Spurenbestimmung von Eisen in Aluminium und Chrom wird betont.

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MEASUREMENTS IN THE ULTRAVIOLET REGION OF APPARENT ABSORPTION BY BARIUM SULFATE SOLS

by

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The exact relationship between the absorbance of a suspension and the wavelength of incident light depends upon several parameters, and, indeed, extensive theoretical and experimental work has made possible the use of absorption measurements as a method for the estimation of particle size^{1,2,3}. In general, "Tyndall spectra" show an increase in the apparent absorption with a decrease in the wavelength of the source. Recent work by FOG⁴ has shown that one can apply corrections for the presence of turbidity in order to determine the amount of true absorption. He employed a plot of the logarithm of the absorptivity against the logarithm of the wavelength, a plot which HELLER AND VASSY⁵ had pointed out earlier could be used as a means of distinguishing between true and apparent absorption.

This plot results in an approximately straight line over a range of 100 m μ , and has a slope which is dependent upon the average particle size of the suspension. The smaller particles result in steeper slopes. HELLER, KLEVENS AND OPPENHEIMER⁶ established a calibration curve relating particle size to the slope of the log plot for the cases where the refractive index ratio was 1.24 ± 0.01 .

In the present study, absorbance measurements were made in the ultraviolet region in order to take advantage of the increase in scattering at shorter wavelengths as a means of extending the technique to the dilute sols produced for nephelometric measurement. Thus, it was hoped that the technique would provide qualitative information about changes in the average particle size of the barium sulfate sols which in turn would be useful in describing the effects of different variables on the nephelometric sensitivity and the stability of the suspensions. These variables include the method of precipitation, the effect of high concentrations of foreign salts, and changes in ethanol content of the solutions. Because nothing was known about the form of the distribution of particle sizes in the polydispersed sols of barium sulfate, no attempt was made to calculate average particle size. It was realized that other techniques, such as angular-dependence light scattering would be required to provide information about the particle-size distribution⁷.

Another objective of this investigation was to compare the relative sensitivities of absorption measurements in the ultraviolet with nephelometric measurements of 90°-scattered light.

EXPERIMENTAL DETAILS

Apparatus

All spectra were taken on a Cary, Model 11, recording spectrophotometer which was used to record the wavelength region from 350 to 220 m μ in approximately 1 minute. The wavelength was always scanned in the same direction. The 100% transmission line was established with a blank which contained all of the components of the final solutions except sulfate. Matched 10-cm cell were employed.

Data relating the concentration of sulfate to the absorbance were obtained using a Beckman DU spectrophotometer and the same 10-cm cells. These absorbance measurements, including those of the blanks, were taken with reference to distilled water. An appropriate cell correction of the order of 0.007 absorbance unit was applied.

A Model 7 Coleman photonephelometer, equipped with the usual cuvettes, was used for the nephelometric analysis of the calcium chloride solutions. The sensitivity of the instrument was established in terms of Coleman nephelos standards.

Measurements of pH were made with a glass electrode in conjunction with a Beckman Model G pH meter. A Fisher refractometer was employed to determine approximate values of refractive indices of solutions.

Preparation of solutions

Calcium chloride solutions were prepared from the "low alkali" calcium carbonate sold by Mallinckrodt Chemical Works. This reagent-grade chemical was analysed nephelometrically, and, as previously reported⁸, was found to be essentially sulfate-free. Two hundred grams of the calcium carbonate, weighed on a trip balance, were slurried with approximately 500 ml of distilled water. Three hundred and thirty ml of concentrated (37%) hydrochloric acid were added very slowly using both a pipet (100 ml) and a buret to deliver the acid. After the solution had been boiled to expel carbon dioxide, it was cooled to room temperature. Its pH was 2.0.

The solution was filtered through S and S black ribbon filter paper, and distilled water was added to bring the volume to approximately 980 ml. The pH was then adjusted to 1.0 by the addition of a few milliliters of 1:10 hydrochloric acid solution. Finally, the solution was transferred to a 1-liter volumetric flask and brought to exact volume with a pH 1.00 solution of hydrochloric acid. The final solution was 2.00M in calcium chloride (0.200 g CaCO₃ per ml), and had a pH of 0.98.

As previously reported⁸, the acidity of this solution cannot be defined accurately in terms of concentration because of its high ionic strength. It was thought advisable to define its acidity in terms of Δ pH_{1/2} values that have been applied to buffers⁹. To do this, 25.00 ml of the 2.00M calcium chloride solution were diluted to 50.00 ml with distilled water. The change in pH was 0.77 unit instead of 0.30. An analogous experiment, performed by diluting 25.00 ml of the calcium solution to 50.00 ml with a hydrochloric acid solution of pH 1.00, resulted in a Δ pH_{1/2} of -0.17 rather than showing no change. Thus the observed pH value is not a simple function of the concentration of the acid in such systems.

From the 2.00M solution of calcium chloride, two solutions were prepared, each of which was 1.00M in calcium chloride and 20% by volume of ethanol. Before these solutions were brought to final volume with a pH 1.0 hydrochloric acid solution, enough sulfate was added to one of them, in the form of a standard solution of potassium sulfate (containing 125 μ g per ml of sulfate and enough hydrochloric acid to give it a pH of 1.0), to produce a solution with a final sulfate concentration of 10.0 μ g per ml. No sulfate was added to the other solution, but, because of the sulfate impurity in the hydrochloric acid used to dissolve the calcium carbonate, sulfate was present though the amount was estimated to be less than 0.2 μ g per ml. The light scattered by the resulting barium sulfate could be ignored. Concentrations of sulfate between zero and 10 μ g per ml were used to obtain calibration curves in 1.0M calcium chloride and were prepared by mixing the required amounts of these two solutions.

Three solutions were prepared from a standard solution of potassium sulfate (250 μ g per ml) to contain 0, 10.0 and 20.0 μ g per ml of sulfate. Each solution was 0.1M in hydrochloric acid and 20% by volume ethanol. Six solutions, each containing 10.0 μ g per ml of sulfate and 0.1M hydrochloric acid were made at 0%, 10%, 30%, 40%, 50% and 60% by volume of ethanol.

A solution of barium chloride was prepared to be 20% by volume of ethanol, 0.1M in hydrochloric acid and 0.178M in barium chloride.

The alcohol used in the preparation of all of the above solutions was U.S.P. absolute ethanol which was obtained from U.S. Industrial Chemicals Company in pint bottles. When ethanol from larger containers (5 gal) was used, a residual turbidity was found to develop, even in the absence of barium chloride, whenever the ethanol was diluted to 20% by volume with 0.1M hydrochloric acid alone.

Precipitation procedure

The same precipitation procedure was used as in the previous nephelometric study⁸, *i.e.*, solid barium chloride dihydrate crystals (30-40 mesh) were added to a 40.00 ml portion of solution using a small scoop and were dissolved by motor-stirring for a three-minute period. The final concentration of barium chloride was 0.089*M*.

One precipitation experiment was run using the technique of mixing equal volumes of a barium chloride solution and a sulfate solution as recommended by TOENNIES AND BAKAY¹⁰. A 20.00 ml portion of 0.178*M* barium chloride solution was added to 20.00 ml of the 20.00 μg per ml solution of sulfate to produce a final mixture equivalent to those produced with the solid reagent.

Filtration of the solutions prior to precipitation of the barium sulfate was omitted because the Millipore filters previously used⁸ were found to contaminate the solutions with a substance that absorbed below 290 $m\mu$. Fortunately, filtration had been found not to be critical when the concentration of sulfate was greater than 2.0 μg per ml.

RESULTS

Spectral data

Typical curves from the Cary spectrophotometer, obtained for barium sulfate sols produced by 10.0 μg per ml of sulfate, are shown in Fig. 1. The changes in the spectra with time were followed by making successive recordings at convenient intervals of time without disturbing the cells. The time was measured from the moment of addition of the reagent, and therefore included the time required to dissolve the solid barium chloride.

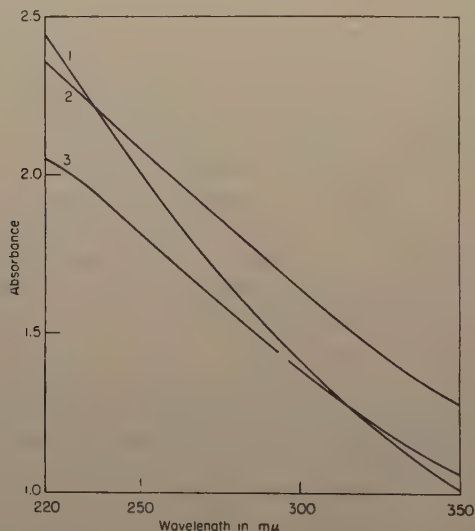


Fig. 1. Spectra of sols produced by 10.0 μg per ml of sulfate.
Curve 1. 20% ethanol after 6 min
Curve 2. 20% ethanol after 74 min
Curve 3. 1.00*M* CaCl_2 , 20% ethanol after 7 min

The effect of the ethanol content at two levels, 10% and 20% by volume, on the spectra produced by sols resulting from a concentration of 10.0 μg per ml of sulfate is shown in Fig. 2 and, in addition, the results for a sol containing no ethanol. This figure summarizes the spectra by showing the absorbances at 230 $m\mu$, 280 $m\mu$, and 330 $m\mu$ as a function of time. At 230 $m\mu$, only a slight increase in absorbance was observed after the first five minutes, and with time the absorbances decreased

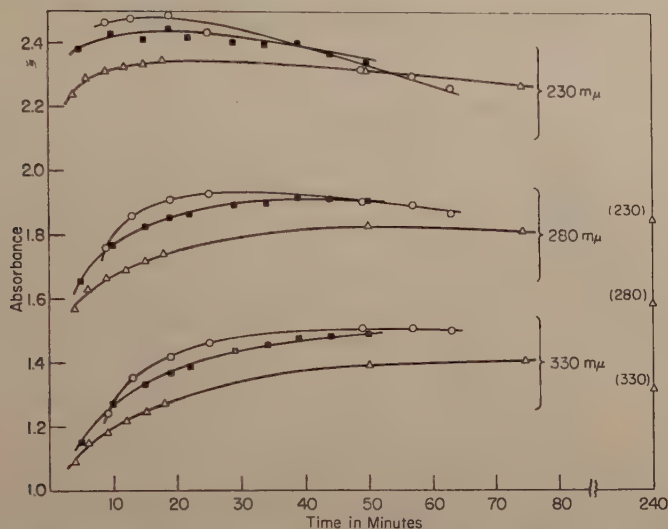


Fig. 2. Effect of different percentages of ethanol on absorbance values as a function of time.

○ 0% ethanol
 ■ 10% ethanol
 △ 20% ethanol

noticeably. At 280 $m\mu$ and 330 $m\mu$, the increase in absorbance continued for a longer time before leveling off. The effect of the ethanol was to lower the initial values of the absorbances, and to cause a more gradual increase in their values. This resulted in a crossover of the 0% and 10% curves especially at the short wavelengths. The points shown at the righthand margin are absorbances of the sol containing 20% ethanol and were recorded 4 hours after precipitation. These values indicated that progressively smaller changes with time were occurring in the absorbance values for the longer wavelengths.

Earlier work⁸ had shown that the use of a solution of barium chloride as recommended by TOENNIES AND BAKAY¹⁰ instead of the solid reagent markedly lowered the sensitivity of the nephelometric measurements for the determination of sulfate. The slope of the nephelometric calibration curves was only 14 "nephelos" units per μg of sulfate when a solution of the reagent was used, whereas a slope of 25 was obtained with the solid barium chloride. Fig. 3 illustrates the striking difference in the absorbance resulting from the use of the two methods of precipitation with sols of barium sulfate which were otherwise identical. When an equal volume of a 0.178M solution of barium chloride was mixed with a solution of 20.0 μg per ml of sulfate (each solution containing 20% ethanol), the absorbance readings were constant from 3 to 15 minutes after mixing and then slowly decreased. This is contrary to the behavior observed for the sols produced by solid barium chloride which showed a pronounced increase in absorbance for the first 20 minutes and, at the longer wavelengths, a slower increase for the next hour. Equally obvious when a solution of barium chloride reagent was used was the lesser dependence of the absorbance on the wavelength which resulted in much lower absorbance values at 230 $m\mu$.

In view of the fact that the present study, as well as the previous nephelometric

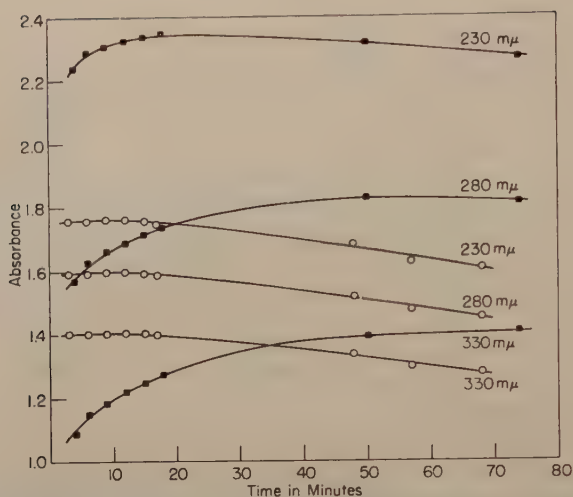


Fig. 3. Comparison of absorbance values obtained by two different methods of adding barium chloride.

■ solid
○ solution

one⁸, was carried out in a room whose temperature was controlled to $24^{\circ} \pm 1^{\circ} \text{C}$, it was deemed advisable to examine the effect of changing the temperature of the solution at the time of precipitation to 15°C and to 35°C . Because much of the nephelometric work had been done on concentrated (about $1M$) solutions of foreign salts⁸, solutions which contained $10.0 \mu\text{g}$ per ml of sulfate, and $1.00M$ calcium chloride were chosen in order to facilitate comparisons.

Fig. 4 shows that the maximum difference between the absorbance values at two different temperatures, after the same time, was only about 5% over a range of 20°C , which is quite acceptable for most analytical purposes. However, the magnitude of the change differed with the wavelength, being smaller at longer wavelengths. The differences in absorbance values were not much greater than the experimental variation encountered at a single temperature upon redetermining the spectra for replicate samples at 24°C .

A comparison of the curves in Fig. 4 with those in Fig. 3 (for solid reagent) shows that the presence of calcium chloride in the solution markedly increased the stability of the sols, though their absorbances were decreased by about 20%. As will be pointed out later, this decrease was only about one-third of that observed nephelometrically.

Interpretation of spectral data

Observations of absorbance as a function of wavelength have been used by BARNES AND LAMER¹ for determining the particle size of sulfur sols, and involves a comparison of experimental data with theoretically calculated curves. However, the applicability of the comparison is limited to particles of spherical or nearly spherical shape². Therefore, because the shapes of particles of barium sulfate produced by typical precipitation are non-spherical¹¹, and because nothing was known about the form of the distribution of particle sizes to be expected with the polydispersed sols of

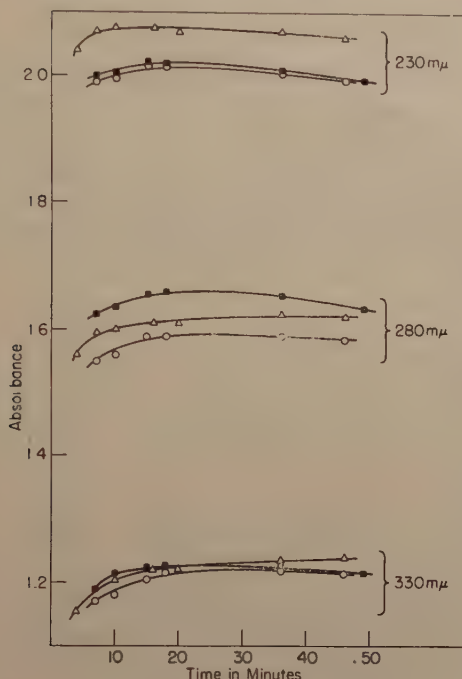


Fig. 4. Effect of temperature on absorbance values of sols produced in solutions containing 1.00M calcium chloride as a function of time.

Δ 35°
○ 24°
■ 15°

barium sulfate obtained in this investigation, no attempt was made to calculate the values of average particle size from the absorbance data. Furthermore, in order to obtain data for comparison with the more readily calculable values from light-scattering theory, a low ratio of particle diameter to wavelength should be used. This would appear to require the use of wavelengths longer than the ultraviolet.

HELLER AND VASSY⁵ have suggested that the change of relative particle size in an inorganic colloidal sol can be followed as a function of time from the slopes obtained by plotting for successive spectra the logarithm of the absorptivity against the logarithm of the reciprocal of the wavelength. When this type of plot was made for each of the spectra taken with a particular barium sulfate sol, the resulting curves were practically linear over the range of wavelengths from 230 mμ to 330 mμ. The average slope of each log plot was estimated by drawing a straight line between the points at 260 mμ and 300 mμ. Fig. 5 shows the slope of each log plot as a function of time, and each curve represents the kinetics of the changes in relative average particle size for each sol. As the average particle size becomes larger, the slope of the log plot decreases, *i.e.*, the absorbance becomes less dependent upon the wavelength.

Curve 1, taken from the spectra obtained for the barium sulfate sol produced with solid reagent in 20% ethanol, shows that there was a rapid change in average particle size during the first 30 minutes. Curve 5, plotted from the spectra of sols resulting from the use of solution reagent, may be compared directly with Curve 1

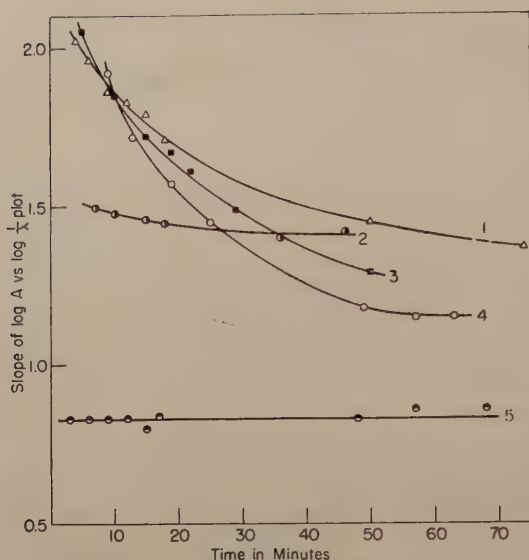


Fig. 5. Kinetics of changes in relative average particle size.

1. Δ 20% ethanol, solid reagent
2. \bullet 20% ethanol, 1.00M CaCl_2 , solid reagent
3. \blacksquare 10% ethanol, solid reagent
4. \circ 0% ethanol, solid reagent
5. \bullet 20% ethanol, solution reagent

Refractive indices for these solutions are 1.34₄, 1.37₀, 1.34₂, 1.33₈, and 1.34₄ for curves 1-5 respectively.

because the final chemical composition of each solution was identical. It is evident that the average particle size produced by the use of the solution of barium chloride was much larger than that produced by the use of crystals. Furthermore, practically no change in average particle size occurred with time as a result of using the solution of barium chloride, whereas the use of the solid reagent resulted in a rapid increase in the average particle size during the first 30 minutes. Although the slope of Curve 5 was constant with time, Fig. 3 shows that the absorbance values decreased slowly but uniformly at all three wavelengths after the first 15 minutes. This would seem to indicate that settling of the particles rather than an increase in average particle size was occurring in these solutions.

Curve 2 shows that 1.00M calcium chloride greatly reduced the rate of increase of the average particle size. The fact that the magnitude of the slopes of this log plot fell below those of Curve 1 cannot be attributed unambiguously to a larger average particle size because of the difference in the refractive indices of the solutions — and possibly in the refractive index of the solid barium sulfate because of coprecipitation from the concentrated solutions of calcium chloride.

Curves 3 and 4 were calculated from the spectra for sols precipitated in the presence of 10% and 0% ethanol respectively. Together with Curve 1, for 20% ethanol, these curves show that the rate of change of particle size increased with decreasing alcohol content. Because of the small differences in the refractive indices, one is also relatively safe in extending the interpretation of the curves to a comparison of the relative average particle sizes in the three solutions.

Relationship between absorbance and concentration of sulfate

The large absorbance resulting from a sol produced from 10.0 μg per ml of sulfate suggested the possibility of determining sulfate by its apparent ultraviolet absorption. Furthermore, a comparison of Figs. 3 and 4 indicated that the presence of 1.00M calcium chloride did not decrease the absorbance of the solutions nearly as much as it did the nephelometric reading (from 25 to 10 nephelos units per μg of sulfate⁸). As a result, as shown in Fig. 6, calibration curves were established at three wave-

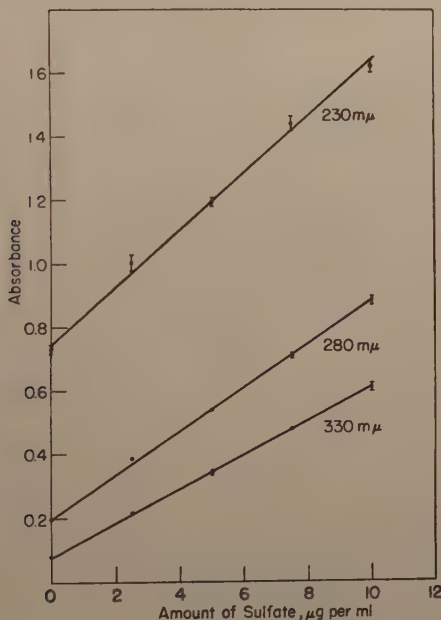


Fig. 6. Calibration curves at three wavelengths for 0-10 μg per ml of sulfate in 1.00M calcium chloride and 20% ethanol.

lengths (230 mμ, 280 mμ, and 330 mμ) with a series of solutions covering a concentration range from 2.5 to 10.0 μg per ml of added sulfate. Each point used to establish the curves was obtained 30 min after precipitation, and was the average of duplicate measurements. The range of the duplicates is indicated on the figure. These same solutions when read on the nephelometer produced values which agreed, within the previously reported limits, with the earlier data⁸.

To explore further the reproducibility of the measurements, five replications of the absorbance measurements were made at sulfate concentrations of 5.0 μg per ml and 10.0 μg per ml for each wavelength. Table I shows the average values obtained after subtracting the blank readings. It is evident from a consideration of Fig. 6 that the slope of the calibration curve at 230 mμ, though greater, is less certain than at the longer wavelengths.

A constant slit width was maintained at each wavelength for the readings used in establishing a particular calibration curve. However, it was found that the readings were quite independent of the slit width so that any slit width, which would permit the instrument to be balanced against the reference cell, could be used. Furthermore,

TABLE I

CORRECTED FOR THE BLANK, ABSORBANCE READINGS, OF FIVE SAMPLES AT EACH OF TWO CONCENTRATIONS OF SULFATE

Sulfate μg per ml	5.0			10.0		
	330	280	230	330	280	230
Wavelength in $m\mu$						
Average absorbance	0.263	0.343	0.459	0.539	0.686	0.887
Standard deviation of absorbance	0.005	0.003	0.011	0.010	0.010	0.016
Coefficient of variation of absorbance	1.9	0.9	2.4	1.9	1.5	1.8

it was shown that adjustment of the wavelength setting on the Beckman from either the high or low wavelength direction did not influence the absorbance readings.

It is evident from a comparison of the absorbance values taken on the Cary with those taken on the Beckman (Figs. 2 and 6) that the same solutions produced much larger readings on the Cary even though those readings were referred to a true blank, whereas the Beckman values were referred to water and therefore included the absorbance of the blank. This difference is undoubtedly due to instrument design. LOTHIAN AND CHAPPEL¹² have indicated how absorbance readings depend upon the solid angles through which the source and the detector view the sample. Higher absorbances are obtained when these angles are only a very few degrees removed from 0° . Because the amount of light scattered in the forward direction will be greater for larger particles, the smaller absorbance values obtained with the Beckman indicate that its receiver may view a large solid angle. The presence of more stray light in the Beckman could also contribute to such a difference.

The absorbance readings for 0.0 μg per ml of sulfate in Fig. 6 can be accounted for by the presence of the soluble inorganic salts as shown in Table II. As will be mentioned later, this additivity will make possible the analysis of general unknowns.

TABLE II

ADDITIVITY OF ABSORBANCES OF THE COMPONENTS OF THE BLANK

Wavelength in $m\mu$	330	280	230
Absorbance of 1.00M CaCl_2	0.067	0.174	0.671
Absorbance of 0.089M BaCl_2	0.008	0.022	0.068
Calculated total	0.075	0.196	0.739
Observed total	0.074	0.197	0.734

Comparison of absorbtimetric and nephelometric data

In order to explore further the effect of the concentration of ethanol on the stabilities of the sols, a brief nephelometric study was made covering the range from 0-60% by volume. The data in Fig. 7 were obtained on solutions which contained 10.0 μg per ml of sulfate but no foreign salt, the presence of which would have tended to stabilize the readings. Ten minutes after the addition of the solid barium chloride, all the curves decreased with time. In general, the rate of decrease for the "nephelos" reading was smaller for larger concentrations of ethanol, as well as the magnitude of the reading. The solution containing 10% ethanol proved to be an exception to the

latter observation by producing the highest "nephelos" values. The 20% ethanol solution was also an exception for time intervals greater than 80 minutes, the point at which it crossed the 0% curve.

A comparison of the nephelometric data in Fig. 7 with the absorbance-time curves in Fig. 2 for 0%, 10% and 20% of ethanol shows no simple correlation. It is apparent that up to 30 minutes after precipitation, the solution containing no ethanol had the highest absorbance values at all three wavelengths. Furthermore, the absorbance of the solution increased long after the 90°-scattered light began to decrease. The closest correlation between the nephelometric and the absorbtimetric data occurred at 230 $m\mu$.

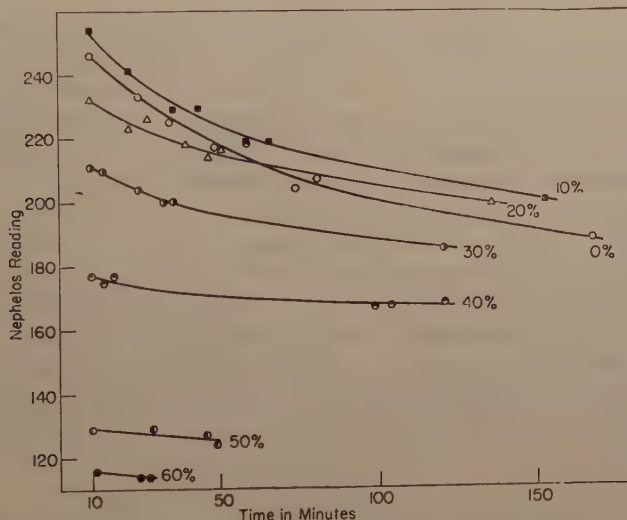


Fig. 7. Effect of different percentages of ethanol on nephelometric values as a function of time.

However, qualitative agreement was obtained when the rates of decrease of the nephelometric values were compared with the rates of increase of the relative average particle sizes calculated from the absorbance-time measurements. As shown by a comparison of Fig. 7 with Fig. 5, the least stable nephelometric readings were obtained on the solutions containing the least amount of ethanol, and these solutions showed the most rapid increase in average particle size with time. Likewise, the stability of the nephelometric measurements for barium sulfate sols in the presence of 1.00M calcium chloride⁸ was directly attributable to the slow rate with which the average particle size increased. Furthermore, the very striking difference between the spectra obtained from the sols precipitated by means of a solution of barium chloride and those precipitated by solid crystals confirmed the distinct difference which had been observed nephelometrically. Use of the solution of reagent resulted in an initial average particle size which was relatively much larger than that obtained when solid reagent was used. Thus, the difference in the nephelometric slopes obtained by the two precipitation techniques (14 "nephelos" units per μg of sulfate for the solution of barium chloride; 25 "nephelos" units per μg of sulfate for the

crystals) was the result of a decrease in the amount of 90° -scattered light and an increase in the forward scattering resulting from the larger average particle size.

Although the stabilities of the absorbance readings were greater when precipitations were made by mixing solutions rather than by dissolving solid reagent, one should not infer that the reproducibilities of the former were better. In fact, the opposite has been shown to be true⁸. The reproducibility was even poorer when the sulfate solutions contained high concentrations of foreign salt.

Of practical importance was the fact that absorption measurements in the ultraviolet region provided sufficient sensitivity to sols of barium sulfate to suggest the possible use of such measurements as a substitute for nephelometry. The present paper indicates that absorbance could indeed be measured on very dilute sols but that larger volumes of solution were required for absorbance measurements in order to obtain comparable sensitivities. A coefficient of variation of approximately 1.7% for a level of 10.0 μg per ml (see Table I) was essentially the same as that previously reported for the nephelometric procedure⁸. However, absorbance measurements were advantageous in the presence of 1.00M calcium chloride because the reading for 10 μg per ml of sulfate was 80% of the value obtained in its absence. Nephelometrically, the reading fell to 40% of its former value.

An evaluation of the effect of the temperature of the solution on the nephelometric measurements of the sols of barium sulfate formed in the presence of 1.00M calcium chloride, was also made. The readings (in nephelos units) were 101.2 at 35°C , 96.0 at 24°C and 94.2 at 15°C . This overall change amounted to about 7% and agreed well with the temperature effect observed for absorbance measurements at the shorter wavelengths. With either nephelometric or absorbtimetric measurements, changes of $\pm 5^\circ\text{C}$ are not important.

DISCUSSION

The sensitivity of turbidimetric measurements in the ultraviolet region, using 10-cm cells, is sufficiently great to permit the measurement of sulfate concentrations which are usually handled nephelometrically. If this technique were to be used for the determination of sulfate, the interference of chemically absorbing species would have to be determined. It is possible, in the presence of low levels of absorbing species, that an analysis could be accomplished by measuring first the absorption of the sample solution before the addition of barium chloride and then the change in the absorption upon formation of the precipitate. Assuming the additivity of absorbances to be valid, the absorbance of the blank could be estimated by determining, in addition, the absorbance of the barium chloride (in the solvent mixture used) and adding it to the absorbance of the solution before the precipitation, as was done in Table II. Finally, the change in the absorbance per μg of sulfate, *i.e.*, the slope of the calibration curve, could be determined by the method of standard addition.

In some cases, a more direct estimation of the blank could be made by precipitating and filtering off the barium sulfate and then measuring the absorbance of the solution. However, in order to use this procedure, one would have to be certain that the filtering medium did not alter the solution itself and that the suspension was completely removed by the filtration.

ACKNOWLEDGEMENT

The authors are indebted to the Atomic Energy Commission for partial support of this study.

SUMMARY

Absorbance measurements in the ultraviolet have been shown to be useful for following changes with time in the average particle size of barium sulfate sols. The effects of the method of adding the barium chloride, a change in the temperature, the presence of 1.00M calcium chloride and the percentage of ethanol in the solution have been examined as a function of time. By measuring the apparent absorbance of barium sulfate sols in 10 cm cells, sulfate can be determined in the range of 2.5-10.0 μg per ml. This is a range which, in the past, has had to be handled by nephelometry.

RÉSUMÉ

Des mesures de l'absorption dans l'ultra-violet ont été effectuées pour suivre l'évolution de la grosseur moyenne des particules des sols de sulfate de baryum. L'influence de la méthode d'addition du chlorure de baryum, d'un changement de température, de la présence de chlorure de calcium 1.00M et de la concentration en alcool éthylique dans la solution a été examinée en fonction du temps. En mesurant l'absorption apparente des sols de sulfate de baryum dans des cuves de 10 cm, on peut doser des quantités de sulfate allant de 2.5 à 10 μg par ml. Ce sont là des concentrations qui, par le passé, devaient être mesurées par néphélométrie.

ZUSAMMENFASSUNG

Es wurden Ultraviolett-Absorptionsmessungen ausgeführt, um das Zunehmen der mittleren Teilchengrösse von Bariumsulfatsolen zu verfolgen. Der Einfluss der Zugabemethode des Bariumchlorides, einer Temperaturänderung, der Gegenwart von 1.00M Kalziumchlorid und der Konzentration an Äthylalkohol in der Lösung wurde in Funktion der Zeit untersucht. Wenn man die scheinbare Absorption der Bariumsulfatsole in einer Zelle von 10 cm misst, kann man Sulfatmengen in der Grössenordnung von 2.5 bis 10 μg per ml bestimmen. Das sind Konzentrationen, die bisher durch Nephelometrie gemessen werden mussten.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE IV. THE USE OF THE ALUMINIUM-ERIOCHROME CYANIN COMPLEX

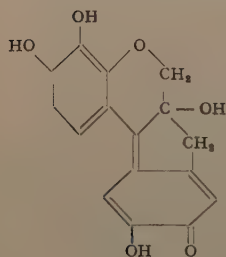
by

B. J. MACNULTY,* G. J. HUNTER AND D. G. BARRETT

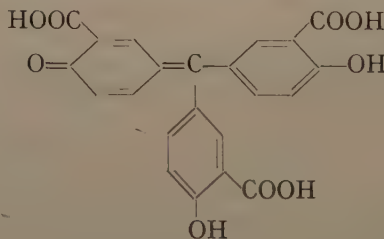
Chemical Inspectorate, British Ministry of Supply, Station Approach Buildings, Kidbrooke, London, S.E.3 (England)

INTRODUCTION

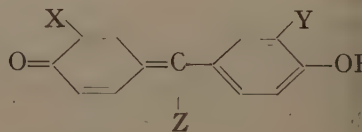
The determination of fluoride in microgram amounts is of necessity carried out by means of a secondary effect since the element itself forms no known suitable coloured ions or complexes. Most successful methods for fluoride determination have been based on the destruction by fluoride of a coloured complex, the fading of colour so produced being in many cases proportional to the concentration of the ion. In a previous paper^{1,2} a method for determining fluoride using the complex between aluminium and haematein was described. In this paper it was mentioned that the aluminon-aluminium complex also showed a similar but very much less sensitive effect. From this work it was clear that an even more sensitive method could be developed if a dye aluminium complex of sufficiently high molecular absorbandy and a sensitivity to fluoride equal to that of the aluminium-haematein complex could be found. Consideration of the structure of haematein(I) and auramine tricarboxylic acid (aluminon)(II) indicated that a compound containing a structure of the type III would be likely to form a suitable complex with aluminium, type III being the essential component common to both I and II.



I



II



III

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Two dyestuffs which possess this structure have been recently used in connection with the determination of fluoride, namely eriochrome cyanin R (IV) which was used by THRUN³ as the aluminium lake, by MEGREGIAN⁴ as the zirconium lake and by SAYLOR AND LARKIN⁵ as an indicator in the titration of fluoride with aluminium chloride, and chromazurol S (V) which was used by MILTON⁶ as the indicator in titration of fluoride with thorium nitrate. THRUN's method used far too great a quantity of dye and the sensitivity appeared to be disappointingly low, but that of MEGREGIAN which was published after the completion of the present work is of the order of sensitivity expected. The molecular absorbancies for the aluminium complexes of the four dyes (I, II, IV, V) have been determined and are shown in Table I. The figures indicated that both eriochrome cyanin and chromazurol S should be superior to haematein for the determination of fluoride.

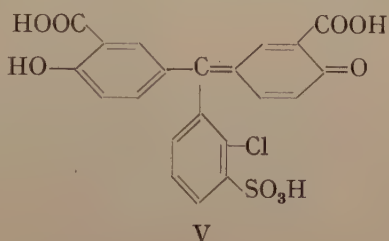
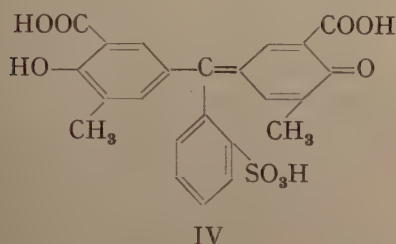


TABLE I

<i>Aluminium complex with</i>	<i>Molecular absorbancy</i>
Aluminon	12,000
Haematein	33,000
Chromazurol S	44,000
Eriochrome cyanin R	88,000

Preliminary experiments indicated that in fact the chromazurol complex was only a little more sensitive to fluoride whereas the eriochrome cyanin R complex was at least three times more sensitive than the haematein complex.

The use of eriochrome cyanin as a reagent for aluminium was fairly extensively studied some twenty years ago by EEGRIWE⁷, by ALTEN^{8,9}, by MILLNER¹⁰ and by RICHTER^{11,12}, who also made some attempt to determine fluoride with the aluminium lake. The findings of these authors indicated that pH control was critical and that at least two forms of eriochrome cyanin existed, one of which reacted readily with aluminium and the other which did not react or only very slowly. A spectrophotometric study of the eriochrome cyanin and its aluminium complex at various pH's was therefore undertaken. Previous work on dye-aluminium systems^{1,2} coupled with the findings quoted by German workers⁷⁻² indicated that a pH in the region of 4.2-5.0 would be most suitable for developing a method for fluoride determination and special attention was given to this range of pH in the present investigations.

EXPERIMENTAL

From the previous work with haematoxylin¹ the approximate concentration of aluminium required for a method for determining microgram amounts of fluoride was known and this governed the amounts of the other reagents to be used. Preliminary experiments showed that the eriochrome cyanin was quite stable at pH 2 but in the region 4.0-6.5 it was unstable, and that the form in which it was present was different since the absorption peak changed from 4800 Å

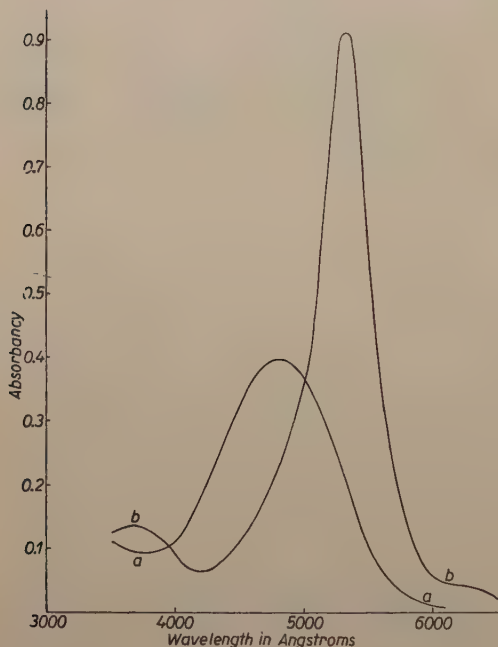
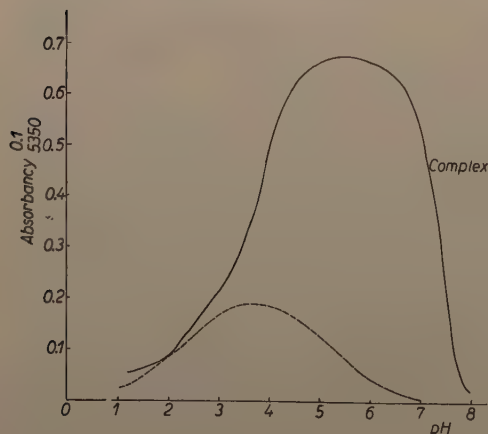


Fig. 1. Spectra of eriochrome cyanin (a) and the eriochrome cyanin-aluminium complex (b).

(a) Eriochrome cyanin at pH 2 $3.7 \cdot 10^{-5} M$.

(b) Eriochrome cyanin-aluminium complex at pH 4.5 $1.64 \cdot 10^{-5} M$.

Spectra plotted on a Unicam Spectrophotometer using a 1 cm cell.



to 5200 Å. In view of this behaviour the dye was kept in solution which was 0.01M with respect to hydrochloric acid. The peak of the aluminium eriochrome cyanin complex was found to lie at 5350 Å and the complex in contradistinction to dye alone was quite stable. Fig. 1 shows spectra of dye alone at pH 2 and complex at pH 4.6.

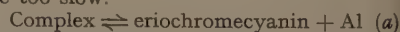
Addition of various amounts of aluminium to a fixed amount of the eriochrome cyanin showed that no further colour was produced by increasing the aluminium concentration when the ratio of dye to aluminium in the complex was two. Job's method of continuous variation gave the same result.

Detailed studies on the effect of pH on the dye, and on the dye aluminium complex were carried out as follows.

200 ml of water and 1 ml of concentrated acetic acid and 10 ml of 2.5M hydrochloric acid were placed in a beaker giving a pH of 1.01. 555 µg of aluminium (as aluminium ammonium sulphate) and 9 ml of eriochrome cyanin (0.25% in 0.01M HCl) were added. The pH was adjusted to the desired value, using a pH meter, by the addition of 1.8M ammonium hydroxide and the absorbance measured in a 0.1 cm cell at 5350 Å after each addition, the values obtained being corrected for volume changes. A similar experiment, without the addition of the aluminium was also carried out.

The results (shown in Fig. 2) confirm the findings of previous authors that satisfactory complex formation takes place at pH between approximately 4.2 and 7.0 and that the intensity of the residual eriochrome cyanin colour diminishes towards the higher pH values.

Now for a satisfactory method of determining fluoride the complex must not be too stable and the rate of the reaction shown in Equation (a) must not be too slow.



These conditions are likely to be fulfilled at pH values which are not quite optimum for complex formation, *i.e.*, between 4.0 and 5.0 and between 6.8 and 7.2. Obviously the higher values of pH are unsuitable as

Fig. 2. Variation of complex formation with pH.
Dye alone — — — — —
Complex —————

aluminium may tend to precipitate and a pH within the lower of the suggested ranges has been chosen.

An attempt was then made to determine fluoride at pH 4.9 (the value already found satisfactory in the case of the aluminium-haematoxylin method) using a solution of complex prepared in the manner already described. The effect of fluoride on the complex was, however, very slow probably due to the slow rate at which the system came to equilibrium; nevertheless the effect produced after 12-16 hours was considerably greater than the effect obtained with the aluminium-haematein complex. The time required was however too long for a successful method and attempts were made to shorten the time taken for the system to approach equilibrium. Reduction of pH, as expected, produced some improvement but to shorten the time to one hour at room temperature it was necessary to go down to a pH of 4, at which value the equilibrium of Equation (a) was so far over to the right that the sensitivity of the method was considerably impaired.

The position at this stage may be summarized as follows:

- (a) Eriochrome cyanin solutions could be kept satisfactorily at low pH (ca. 2.0).
- (b) Stock solutions of eriochrome cyanin-aluminium complex could be prepared which were stable indefinitely.
- (c) Reactions between such stock solutions and fluoride ions were of great sensitivity but the time factor was unsatisfactory.

The obvious way of increasing the rates of reactions involved between fluoride and the dye-aluminium complex was to raise the temperature and experiments at higher temperatures were therefore undertaken.

Effect of temperature on the fluoride-aluminium-eriochrome cyanin system

It was found that when solutions containing various amounts of fluoride and a fixed amount of stock solution (prepared in a manner similar to that described in the section headed "Method") were heated at 35° C a reproducible reaction occurred in solutions containing approximately 22 μg Al/50 ml and that the reaction was substantially complete in about two hours. It was found also that provided the concentration of acetate (used as buffer) was low the blank containing no fluoride was also stable. Unheated blanks were stable also in the presence of a somewhat higher concentration of acetate.

The experiments were repeated at 60° C when it was found that reaction was complete in 15 minutes. In order to avoid complications arising from different rates of heating and cooling, all solutions were made up to a constant volume before heating and cooled down to near room temperature in a cold water bath.

A test method in which fluoride was added to stock solution of complex at pH 4.9, the solution made up to standard volume, heated at 60° C for 15 minutes and then cooled in cold water to room temperature gave good reproducible results but the response to fluoride was not linear, but a similar experiment at pH 4.5 resulted in considerable improvement and calibrations in these conditions approximated very closely to a straight line.

Determination of test samples of fluoride under these conditions gave recoveries of 93% (Table II).

TABLE II

RECOVERY OF FLUORIDE (μg) FROM H_2SO_4 SOLUTION BY DISTILLATION AND DETERMINATION WITH ALUMINIUM ERIOCROME CYANIN COMPLEX

Fluoride added	Fluoride found	% Recovery	Fluoride added	Fluoride found	% Recovery
0	0	—	50	48	96
0	0	—	60	54	90
0	0	—	80	72	90
0	0	—	100	92	92
15	14.1	94	100	93	93
30	29	96	100	93	93
50	46	92			
Mean Recovery 92.7%					

Effect of change of ionic strength on the complex

Since many distillates for fluoride determination contain large quantities of free acid it is necessary to ensure that the effect of an increase in ionic strength in a solution of complex will be small. Experiments showed that increasing the ionic strength of a solution of eriochrome cyanin-aluminium complex resulted in a decrease in complex concentration which was approximately proportional to \sqrt{I} for a small increase in I (Table III). The pH control, of course, was also

affected, a significant decrease in pH occurring in the solutions of higher ionic strength. An obvious remedy was to increase the ionic strengths of all solutions. This was done by making the stock solution 0.5*M* and the buffer solution 2*M* with respect to ammonium chloride. Attempts were made to make the stock solution 1*M* with respect to ammonium chloride but these resulted in some precipitation of the complex. The addition of salt resulted in a decrease in total complex concentration which was compensated by increasing the amount of stock used in the fluoride determination.

TABLE III

THE EFFECT OF IONIC CONCENTRATION I ON THE ABSORBANCY OF ERIOCHROME-CYANIN-ALUMINIUM COMPLEX SOLUTIONS (STANDARD STOCK SOLUTION USED)

<i>I</i>	\sqrt{I}	Salt KCl Δ Absorbancy	pH	Salt NH ₄ Cl Δ Absorbancy	pH
0.004	0.0632	0	4.56	0	4.56
0.084	0.29	0.107	4.47	0.128	4.47
0.164	0.405	0.175	4.44	0.214	4.43
0.324	0.57	0.261	4.42	0.314	4.40
0.644	0.8	0.328	4.40	0.419	4.36
1.28	1.13	—	—	0.463	4.32

The addition of salt to stock and buffer solutions also resulted in improved pH control. Recoveries of fluoride by distillation as hydrofluosilicic acid and determination using the new technique now gave recoveries close to 100% (Table IV).

TABLE IV

RECOVERY OF FLUORIDE (μg) FROM H_2SO_4 SOLUTION BY DISTILLATION AND DETERMINATION WITH ALUMINIUM-ERIOCHROME-CYANIN COMPLEX USING SOLUTIONS OF INCREASED IONIC STRENGTH (0.8)

Fluoride added	Fluoride found	% Recovery	Fluoride added	Fluoride found	% Recovery
0	< 1	—	30	29	97
0	0	—	30	30	100
0	0	—	30	30	100
20	20	100			
30	30	100	35	36	103
Mean Recovery 100%					

Effect of pH on eriochrome-cyanin

In parallel with the experiments on the effect of temperature and ionic strength an investigation into the behaviour of eriochrome-cyanin with pH and its reaction with aluminium under these conditions was started.

Two solutions of 0.01% eriochrome-cyanin were prepared by dilution of the 0.25% solution used for the method and the pH adjusted to 4.6 and 2.0 respectively. These solutions were diluted to 0.002% and the spectra recorded immediately using a Unicam spectrophotometer and 1 cm cells. Change of spectra were recorded with time over several weeks, the solutions being kept at room temperature (Fig. 3). It was found that the dye at pH 2.0 has an absorption peak at 4800 Å and this is perfectly stable, showing no change over a period of five months. The solution of dye at pH 4.6, which had an absorption peak at 5200 Å, underwent a rapid change (Fig. 3), the peak height falling off to less than half its original height in 24 hours (Curve D, Fig. 3). No further decrease in peak height at 5200 Å was detected even after five months; a spectrum plot gave a curve identical with D.

Further investigation of the eriochrome-cyanin at pH 4.6 showed that heating to 60° C increased the rate of decrease of absorbancy at 5200 Å but made no difference to the final figure obtained (Curve D). The rate of decrease was independent of dye concentration for solutions containing 0.002%-0.05% eriochrome-cyanin. When the pH of the solution of aged (faded) dye was changed from 4.6 to 2.0 and then restored to 4.6 it was found that the height of the absorbancy peak at

5200 Å had returned to its original value. The peak height proceeded to decrease with time as previously observed. This process of regeneration and decay of the original form of eriochromecyanin at pH 4.6 could be repeated indefinitely.

Freshly prepared dye at pH 4.6 reacted rapidly with aluminium giving a maximum absorbancy at the complex peak 5350 Å after ten minutes, whereas aged dye of the same pH reacted only very slowly, the reaction taking approximately eighteen hours to reach completion.

Complete spectra of the dye solutions at pH 2.0 and 4.6 were recorded on a

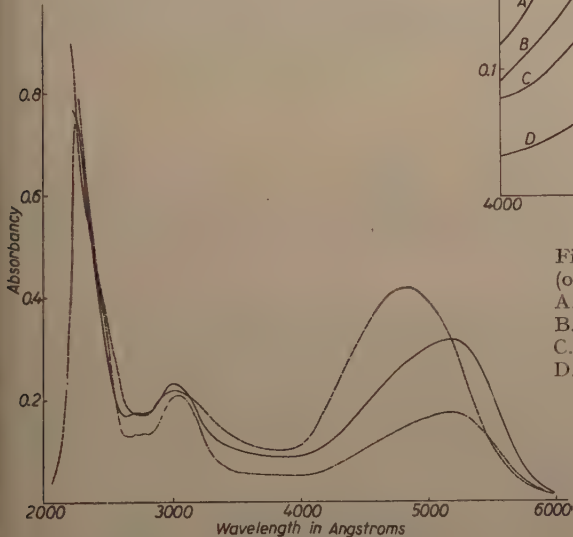


Fig. 4. Spectra of eriochromecyanin.
Freshly prepared 0.002% dye pH 4.6 ———
Aged 0.002% dye pH 4.6 - - - - -
0.002% dye pH 2.0 - · - · -

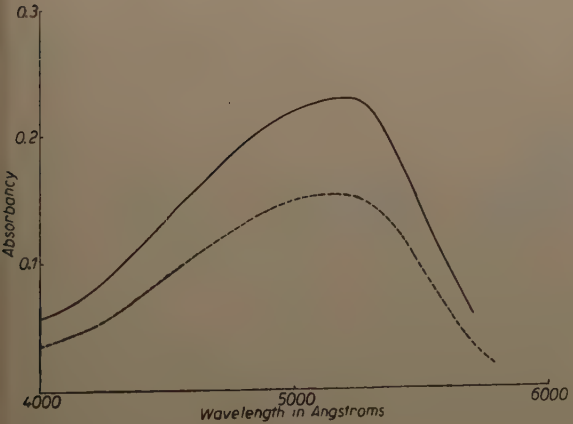


Fig. 5. Spectra obtained after complete destruction of complex by fluoride.
Spectrum recorded immediately —
Spectrum recorded after 1 day - - -

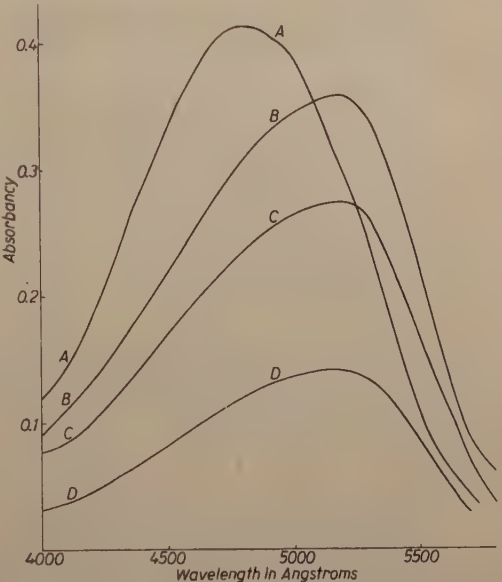


Fig. 3. Spectra of eriochromecyanin (0.002% solution).
A. pH 2.0
B. pH 4.6 Freshly prepared
C. pH 4.6 Age 6 h
D. pH 4.6 Age 24 h

Hilger Uvispec spectrophotometer using a one centimetre cell and the results are shown in Fig. 4.

The spectrum of the dye obtained by complete destruction of the aluminium complex by fluoride is shown in Fig. 5. The spectrum corresponds to that of an aged dye which has nearly completed the aging process, and on standing the absorbancy decreases to the expected figure (corresponding to curve D, Fig. 3).

METHOD

- A. Reagents
- (i) *Standard fluoride solution*
Dissolve 0.5525 g of sodium fluoride in water and dilute to 250 ml. Dilute 1 ml of this solution to 100 ml.
1 ml = 10 µg F.

Fig. 5. Spectra obtained after complete destruction of complex by fluoride.
Spectrum recorded immediately —
Spectrum recorded after 1 day - - -

The purest available material should be used; that supplied by BAKER AND ADAMSON to A.C.S. specification is suitable.

(ii) *Standard aluminium solution*

Dissolve 1.867 g 'AnalaR' quality aluminium ammonium sulphate ($\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in water and dilute to 100 ml.

1 ml = 1.11 mg Al.

For use dilute 10 ml of the above solution to 100 ml.

1 ml = 111 μg Al.

(iii) *Eriochrome cyanin solution 0.25%*

Dissolve 0.25 g of solid in 10 ml of 0.1M hydrochloric acid and dilute to 100 ml.

(iv) *Ammonium hydroxide 9M.*

(v) *Glacial acetic acid.*

(vi) *Buffer solution (pH 4.5)*

Dissolve 32 g 'AnalaR' quality ammonium chloride in 220 ml of water. Add 25 ml of glacial acetic acid and 7.5 ml of concentrated ammonia (sp.gr. 0.88). Cool to room temperature and adjust pH to 4.5 by further addition of ammonia using a pH meter. Dilute to 300 ml and filter.

B. *Procedure*

(a) *Preliminary treatment*

Separate the fluoride from interfering ions if necessary by distillation from sulphuric acid in the presence of silica according to the method of WILLARD AND WINTER¹³. Collect 160 ml of distillate. If a micro apparatus such as that described by HORTON, THOMASON AND MILLER¹⁴ and by ourselves¹⁵ is used, only 10-20 ml need be collected. Treat distillate as described below.

(b) *Treatment of distillates*

I. *For distillates of acid content equivalent to <1 ml 1M acid/150 ml*

This applies also to samples where distillation is not necessary, e.g., water.

- (i) Neutralize the distillate to phenolphthalein with 0.1M sodium hydroxide. Record the volume of the neutralized solution and the volume of alkali used.
- (ii) Prepare a blank solution by neutralizing a volume of 0.1M sodium hydroxide equal to that used in step (i) with 0.05M H_2SO_4 using phenolphthalein as indicator. Dilute the solution to a volume equal to that of the neutralized distillate.

II. *For distillates of high acid content*

- (i) Add sufficient 9M ammonium hydroxide to the distillate to bring the pH to 7 and note the volume required. Add 1 ml of glacial acetic acid and adjust the pH to 4.5 by further addition of ammonium hydroxide, and again note volume used.
- (ii) Prepare a blank solution by adding 1 ml glacial acetic acid to a volume of 9M ammonium hydroxide equal to the total amount used in step (i) and dilute to at least 120 ml. Add acid (of the kind present in the distillate) to bring the pH to 4.5. Dilute the solution to a volume equal to that of the neutralized distillate.

(c) *Determination of fluoride*

- (i) Place a suitable volume of the neutralized distillate in a 50 ml flask and an equal volume of blank solution in a second 50 ml flask. Add 2 ml acetate buffer to each flask and mix well.
- (ii) Into each flask pipette 15 ml aluminium-eriochrome cyanin stock solution; make up to the mark with water and mix well.
- (iii) Place flasks in a water bath at 60° C for 15 minutes. Cool to room temperature by immersion in a cold water bath.
- (iv) Measure the difference between the absorbancies of the two solutions using light of wavelength 5350 Å. The Unicam spectrophotometer and a 1 cm cell are recommended for this operation but other suitable instruments may be used.
- (v) Calculate the fluoride present by reference to a prepared calibration graph.

C. *Preparation of aluminium-eriochrome cyanin stock solution*

To 450 ml water in a 600 ml beaker add in order the following, mixing well after each addition:

- (i) 13.4 g ammonium chloride
- (ii) 1 ml glacial acetic acid
- (iii) 20 ml 0.25% eriochrome cyanin solution
- (iv) 10 ml standard aluminium solution (111 μg Al/ml)

Finally add 1.8*M* ammonium hydroxide to bring the solution to pH 4.5 using a pH meter. Make up to 500 ml and filter through a Whatman No. 1 paper. Add one crystal of thymol to prevent mould growth.
The stock solution should be allowed to stand for two or three days before use.

D. Calibration

- (i) Into each of six stoppered measuring flasks (numbered 1-6) of 50 ml capacity pipette 2 ml of buffer solution (pH 4.5).
- (ii) Add standard fluoride solution to the flasks to give fluoride content as follows: —

Flask No.	1	2	3	4	5	6
μg F ⁻	0	4	8	12	16	20
- (iii) Add 30 ml of water to each.
- (iv) Add 15 ml of aluminium-eriochromecyanin stock solution to each, make up to the mark with water and mix well.
- (v) Place the flasks in a water bath at 60° C for 15 minutes.
Then cool to room temperature by placing in a bath of cold water.
- (vi) Measure the difference between the absorbancy of each fluoride containing solution and that containing none, using a Unicam spectrophotometer and a 1 cm cell with light of wavelength 5350 Å.
- (vii) Plot a calibration graph of the difference in absorbancy against fluoride concentration. Two typical calibrations are recorded in Table V.

INTERFERENCES

Since this method is basically the same as the aluminium haematoxylin method it is to be expected that the ions interfering with the present method would be the same. In general this is correct. In two cases, however, the effects are different, namely in the cases of nitrite and phosphate (H₂PO₄) where a concentration of 20 p.p.m. in both cases reduces the sensitivity of the method.

DISCUSSION

A. The method

The two typical calibrations shown in Table V and a series of recoveries under normal conditions of use shown in Table VI give a good idea of the accuracy and reproducibility of the method.

TABLE V
TYPICAL CALIBRATIONS FOR THE ALUMINIUM-ERIOCHROME-CYANIN METHOD

μg F ⁻	0	4	8	12	16	20
Δ Absorbancy · 10 ³ (a)	0	122	234	352	477	580
(b)	0	116	241	347	485	570

The standard deviation of the method is just less than 0.3 at the 3 μg and 11 μg level and 0.68 at the 18 μg level, the overall standard deviation being 0.53. (These figures are taken from a statistical comparison of several methods for fluoride determination which will be fully discussed in Part VI of the present series of papers.) Taking double the standard deviation as giving a 95% probability of a positive result at the detection limit, 0.6 μg should be detectable in 50 ml of final solution. In the case of macrodistillation the amount of distillate after neutralization is of the order of 170 ml and about 30 ml of this can be used for determination; the sample therefore must contain a minimum of 3.6 μg of fluoride. In a macrodistillation

TABLE VI
TYPICAL RECOVERIES OF FLUORIDE (μg) BY THE ALUMINIUM-ERIOCHROME CYANIN METHOD

<i>F⁻ added</i>	<i>F⁻ recovered</i>	<i>F⁻ added</i>	<i>F⁻ recovered</i>
3	3.0	18	18.3
	3.1		18.4
	3.0		17.7
	3.1		17.9
	2.8		18.5
	2.9		18.1
	3.1		17.5
	3.2		17.7
	3.2		17.8
	3.2		17.9
5	5.0	30	30.0
			30.0
11	11.0	40	29.0
	10.9		
	11.4		40.0
	11.2		40.0
	10.8		40.0
	10.7		
	11.1		
	11.1		
	11.0		

apparatus 25 g of sample can easily be handled, giving us a limit of detection for fluoride of about 0.15 p.p.m. Using microdistillation where the whole distillate can be used — and in favourable cases 5 g of original sample — the limit of detection will be about 0.1 p.p.m.

In a recent paper MEGREGIAN⁴ used the complex between eriochrome cyanin and zirconium as a reagent for fluoride. His method possesses the advantage that heating is not necessary, but on the other hand the method is affected by sulphate and when this ion is present even in small quantities the amount must be known. MEGREGIAN states that he can determine fluoride in the range 0.00 to 1.40 mg of fluoride per litre with a standard deviation of ± 0.0163 mg fluoride per litre; the corresponding figures for the aluminium eriochrome cyanin method expressed in MEGREGIAN's terminology as mg of fluoride per litre are, for a range 0.00–0.36 a standard deviation of ± 0.0100 and for a range 0.36–0.60 a standard deviation of ± 0.0230 , the overall standard deviation being 0.0176.

Thus there is little to choose between the two methods. MEGREGIAN's is probably a little quicker to carry out since the heating and cooling required in our method is likely to add about 20 min to the time for a single determination but this would make very little difference where large numbers of samples were being handled; on the other hand the aluminium-eriochrome cyanin method does not appear to be affected by sulphate.

Although MEGREGIAN mentions in his paper that complexes formed between aluminium and fluoride and zirconium and fluoride are $[\text{AlF}_6]^{-3}$ and $[\text{ZrF}_6]^{-2}$, such calculations as can be made from his figures indicate a ratio of one zirconium atom to about one and a half fluorine atoms, which is what we would have expected from the sensitivity of his method. Under the conditions of the aluminium-erio-

chromecyanin method aluminium and fluorine appear to be combined in the ratio of 1:2. The question therefore arises as to the form in which the fluoride is combined with the aluminium (or zirconium), whether all the aluminium released from the complex reacts with fluoride to give compounds of the nature of $[\text{AlF}_y(\text{OH})_{6-y}]^{-3}$ or whether species formed is $[\text{AlF}_6]^{-3}$ with the extra complex being destroyed to maintain some equilibrium between it and an aluminium hydroxide. We are at present investigating this problem further although from the work of BROSETT¹⁶ we would expect the formation of $[\text{AlF}_y(\text{OH})_{6-y}]^{-3}$ (y having values from 1-6).

In the experiments on the fluoride-aluminium-eriochromecyanin system at elevated temperatures the question of the stability of the blanks arose. Completely stable blanks are not of course essential to a method provided they behave in the same way as the sample solutions. In the present case if any reaction involving fluoride (the variable) is virtually complete any subsequent changes in the solution will depend only on the decomposition of the free dye, since it has been found that the complex is quite stable under the conditions of use; and since the decomposition of free dye appears to be independent of the concentration, any slight instability arising from this should affect all readings equally and will therefore not affect the results if the initial conditions of the method are correct.

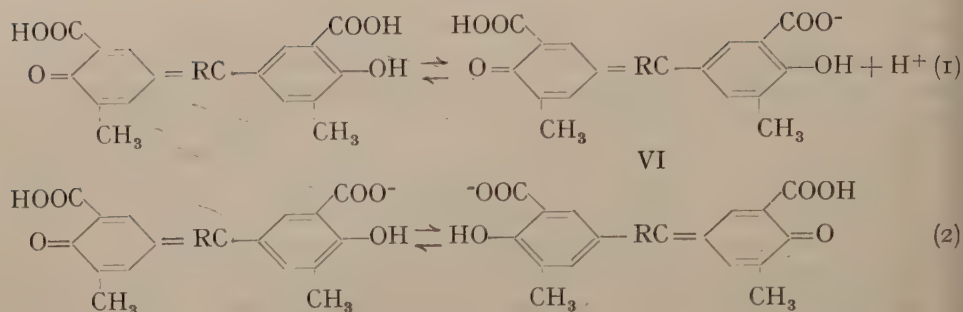
B. Mechanism of reactions involved in the method

The eriochromecyanin was chosen as a likely agent for use, as its aluminium complex, in the determination of fluoride because of its similarity to the basic structure which made haematein and aluminon possible reagents for the same purpose. Hence it would be expected that the reaction mechanisms involved in the present method should be similar to, or at any rate not contradictory to the explanation advanced in the case of haematein.

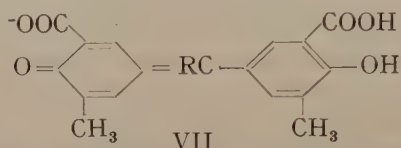
Any explanation of the mode of action of the eriochromecyanin-aluminium complex in the determination of fluoride must cover the following points:

- (i) The ratio of dye to aluminium under the conditions used is 2:1.
- (ii) A satisfactory complex is only formed in the pH region 3.5-7.5.
- (iii) The form of the eriochromecyanin around pH 4.6 differs from that at pH 2 as judged by the absorption spectrum.
- (iv) The form of eriochromecyanin existing around pH 4.6 is unstable and undergoes a change with time (aging).
- (v) Eriochromecyanin freshly brought from pH 2.0 to pH 4.6 reacts rapidly with aluminium whereas after aging the reaction is slow and takes about 18 hours to complete.
- (vi) By taking aged eriochromecyanin to pH 2.0 and then returning the pH to 4.6 the active form of the dye is regenerated, and this process of aging and regeneration can be repeated indefinitely.

The following series of reactions is suggested as covering the above facts. The first stage (Equation 1) is represented by the ionization of the eriochromecyanin: R represents the phenylsulphonate group which is almost certainly completely ionized, this being the grouping which gives the dye its water solubility. The main resonance possibilities of the ion VI are indicated in Equation 2; it will be noted that the ion configuration is essentially the same configuration as that of the active portion of the haematein ion as described in our previous paper².

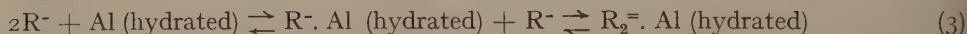


It is probable also that the ion exists in the form



but all these forms are regarded as equivalent, the remaining un-ionized hydrogen not necessarily being bound to the molecule at a specific point.

The second stage of the reaction would appear to be the formation of a chelate compound between the eriochrome cyanin ion and the aluminium, which presumably takes place in two steps, as indicated in equation 3 (where R^- = eriochrome cyanin ion)



As a result of the formation of the complex the essential configuration of the ion is retained and the resonance possibilities are enhanced being extended through the aluminium over two molecules, this increased resonance results in the slight shift of the absorbancy peak of the complex and its high molecular absorbancy.

The form in which the aluminium reacts is of importance in deciding the exact nature of the reactions or series of reactions by which the complex is formed. From our previous work² and such rough calculation as can be made from BROSETT'S¹⁷ latest work, although his conditions are not strictly comparable with our systems, the ion involved would appear to be $\text{Al}(\text{OH})_2^+$ although the ion $(\text{AlOH})^{+2}$ still remains as a possible alternative.

Of the possible structures for the complex only VIII which is similar to the proposed structure of the aluminium salicylate complex would appear from valency considerations to be tenable. This structure then would involve the addition of water

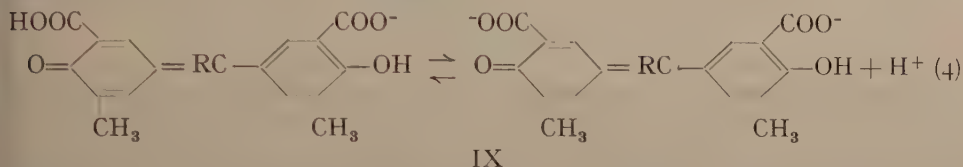


if reaction took place through the $(\text{AlOH})^{+2}$ ion and the addition of hydrogen ion in the case of the $\text{Al}(\text{OH})_2^+$ ion. Unfortunately the present system provides no means of elucidating the problem, though other systems where the reactive dye ion is stable over a greater pH range may provide the answer.

The ageing of the dye to give a form which reacts only very slowly with aluminium provides a problem of some interest. It has been found (see Experimental) that

over a range of concentration of 0.002 to 0.05% eriochrome cyanin the rate of ageing of the dye is independent of the concentration. Hence any reaction explaining this ageing must be first order with respect to the dye and the dye ion, and since on a change of pH from 4.5 to 2.0 the reactive form of the dye is completely re-generated any such reaction must be readily reversible.

It is suggested that the cause of ageing is the slow further ionization of the eriochrome cyanin ion according to Equation 4



and that the ion so formed (IX) is not reactive towards aluminium. Whether any further reaction takes place is not known, but if so, Equation 4 remains the rate controlling step. It is significant that a rough plot of pH against amount of base added to a known quantity of the dye indicates that further ionization takes place in the range of pH in question. The fact that the rate of ageing of the dye, and the rate of complex formation between aged dye and aluminium are both of the same order at room temperature cannot be without significance and must result from the fact that the amount of dye ion formed (Eq. 1) ultimately controls both these reactions.

The reason for the limited pH range over which satisfactory complex formation occurs is due to a combination of two causes, first the range in which the eriochrome cyanin ionizes to give a form suitable for reaction and secondly the pH range in which the aluminium exists as $\text{Al}(\text{OH})_2^+$. BROSETT's figures again indicate that in the region where complex ceases to be formed (pH 6.5-7.5) the amount of aluminium present as $\text{Al}(\text{OH})_2^+$ will be small.

The destruction of complex by fluoride will follow the lines suggested in our previous paper² and since the rate of destruction is of the same order as the rate of ageing of the dye the resultant spectra will approach that of aged dye.

It is realized that this scheme for the mechanism of reaction is only tentative and that further work involving both the aluminium and zirconium complexes with eriochrome cyanin and with chromeazurol S will have to be undertaken to fully elucidate the problem. Such work is being commenced but owing to pressure of other commitments it may be a considerable time before it can be finished and the suggested mechanisms have therefore been outlined in the present paper.

ACKNOWLEDGEMENT

The authors wish to thank Mr. A. S. NICKELSON for his interest and encouragement during the course of this work.

SUMMARY

A spectrophotometric method for determining fluoride using the aluminium-eriochrome cyanin complex is described. Fluoride in solutions free from interfering ions, or obtained by distillation as hydrofluosilicic acid is determined by its destruction of the complex, the amount destroyed being directly proportional to the fluoride content. The method will detect as little as 0.02 $\mu\text{g}/\text{ml}$ of fluoride and with 0-20 μg in the final solution fluoride can be determined with accuracy of $\pm 0.6 \mu\text{g}$.

A preliminary study of the aluminium-eriochrome cyanin-fluoride system has been carried out and a tentative reaction mechanism suggested.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage des fluorures, au moyen du complexe aluminium-ériochromecyanine. L'anion fluorhydrique en l'absence d'ions gênants, ou séparé par distillation comme acide fluosilicique, est dosé par destruction du complexe, la quantité décomposée étant proportionnelle à la quantité de fluorure. Cette méthode permet de détecter jusqu'à 0.02 $\mu\text{g/ml}$ de fluorure. Des quantités de F^- allant de 0 à 20 μg peuvent être dosées avec une précision de $\pm 0.6 \mu\text{g}$. Une étude préliminaire du système aluminium-ériochromecyanine-fluorure a été effectuée et on propose un mécanisme de réaction éventuel.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben, um Fluorid mittels des Aluminium-Eriochromcyanin-Komplexes zu bestimmen. Das Fluorid-Anion wurde in Abwesenheit von störenden Ionen, oder abgetrennt mittels einer Destillation in Form von Fluorkieselsäure durch Zersetzung des Komplexes bestimmt. Die Menge, welche zerstört wurde, war direkt proportional der Menge an Fluor. Diese Methode erlaubt Fluormengen bis zu 0.02 μg nachzuweisen. Mengen von F^- zwischen 0 und 20 μg können mit einer Genauigkeit von $\pm 0.6 \mu\text{g}$ bestimmt werden. Es wurde eine Voruntersuchung des Systems Aluminium-Cyanin-Fluorid ausgeführt und ein möglicher Reaktionsmechanismus vorgeschlagen.

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A RAPID METHOD FOR THE DETERMINATION OF POLYOLS BY DICHROMATE OXIDATION, SPECTROPHOTOMETRIC MEASUREMENT OF Cr(III)

by

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In the course of the development of a procedure for the separation of several polyols from each other by anion-exchange chromatography of their borate complexes¹, it was necessary to determine these compounds in very dilute solution (0.001 to 0.25 mg per ml). Since no reducing agent except the polyol was present, a redox procedure seemed appropriate.

The method of REESE AND WILLIAMS² failed to give results of sufficient accuracy. The method depends upon the addition of a known quantity of dichromate to the sample and the spectrophotometric determination of the excess dichromate by virtue of its reaction with diphenylcarbazide. The instability of this reagent caused some annoyance, but the major errors arose from the fact that quantity of polyol was found as the difference between two larger quantities. The method of CARDONE AND COMPTON³ involves the same undesirable subtraction process, although the use of diphenylcarbazide is eliminated by measuring directly the absorbance of the excess dichromate. Periodate is not a satisfactory oxidizing agent for the small quantities of reducing agent encountered in this problem and also fails to oxidize nonvicinal polyols.

In order to avoid the subtraction step, it is necessary to measure the product of the redox reaction rather than the excess dichromate. Fortunately, Cr(III) has an absorbance maximum in 50% sulfuric acid at 610 m μ , at which wavelength dichromate has a much smaller absorptivity. A method was therefore developed for the determination of polyols by oxidizing them in 50% sulfuric acid with dichromate and measuring spectrophotometrically the resultant Cr(III). Since the absorptivity of Cr(III) is rather small, it was necessary to use cells with a light path of 10 cm.

EXPERIMENTAL

Apparatus and reagents

Absorbance measurements were made with a Beckman quartz spectrophotometer, Model DU, equipped to receive 10-cm silica cells.

The oxidizing reagent is 0.1N sodium dichromate in concentrated sulfuric acid. About 100 g of sodium dichromate dihydrate are dissolved in water and diluted with water to about 100 ml. Five ml of this solution are added to one liter of reagent-grade, concentrated sulfuric acid. Sodium dichromate is precipitated at this point but redissolves on shaking.

Dextrose from the National Bureau of Standards, lot number 4560, was used as a primary standard after being dried for one hour at 100°. Sodium oxalate of primary-standard grade was also dried for one hour at 100°.

Ethylene glycol, 1,2-propylene glycol, and diethylene glycol were obtained from Eastman Kodak. None of them showed any oxidizable impurity in the chromatographic procedure¹. Their water contents, as determined by Karl Fischer titration were respectively 0.24, 0.07, and 0.12%. The glycerol was Baker's Analytical Reagent. The chromatographic procedure¹ revealed no oxidizable impurity and the water content was 4.3% by Karl Fischer titration. 2,3-Butylene glycol of technical grade was obtained from the Celanese Corporation of America. Chromatographic analysis¹ indicated the presence of 8.5% (based on the reducing capacity) of an oxidizable impurity of undetermined nature.* The Fischer titration indicated 0.12% water.

Procedure

Pipet 25.00 ml of sample solution containing not more than one meq of polyol into a flask containing 25.00 ml of the oxidizing reagent. Grasp both flask and pipet in one hand and swirl them vigorously during the addition. The temperature of the mixture rises to about 130°. Similarly prepare a blank by adding 25.00 ml of water to 25.00 ml of the oxidizing solution. Heat the flasks in a boiling-water bath for 15 minutes. Then cool them, and measure the absorbance A of the solution at 610 m μ in a 10-cm cell against the blank as the comparison solution. One blank may serve for several samples that are run at the same time.

RESULTS

With dextrose and sodium oxalate

Five solutions of dextrose of varying concentration and five solutions of sodium oxalate were treated by the foregoing procedure. The results are summarized in the first four columns of Table I.

TABLE I
OXIDATION OF DEXTROSE AND SODIUM OXALATE

No.	Compound	Taken, meq	A	a	Mean a	σ
1	dextrose	0.6900	1.02	0.1478	0.1488	0.00089
2	"	0.5175	0.766	0.1480		
3	"	0.3450	0.513	0.1487		
4	"	0.1725	0.258	0.1496		
5	"	0.06275	0.094	0.1498		
6	sodium oxalate	0.5750	0.853	0.1483	0.1487	0.00056
7	"	0.4312	0.640	0.1484		
8	"	0.2875	0.429	0.1492		
9	"	0.1437	0.213	0.1482		
10	"	0.0522	0.078	0.1494		
Mean of 10 determinations				0.14874		

With polyols

Each of the five polyols was treated by the same procedure. These results are listed in the first four columns of Table II.

Calculations

The absorptivity a was calculated from the absorbances A of the oxidized solutions of dextrose and sodium oxalate by equation (1)

$$a = \frac{A}{10 \text{ } c} \quad (1)$$

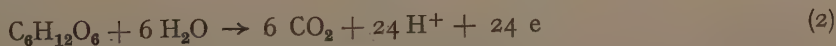
* Later investigation of this sample revealed that the major constituent was meso-2,3-butylene glycol and that the "impurity" was the racemic-2,3-butylene glycol.

TABLE II
 OXIDATION OF POLYOLS

No.	Compound	Taken, mmol*	A	n	Mean n	σ
1	ethylene glycol	0.05077	0.751	9.95	10.03	0.062
2	"	0.03807	0.571	10.09		
3	"	0.02538	0.380	10.07		
4	"	0.01269	0.189	10.02		
5	diethylene glycol	0.03629	1.08	20.01	20.06	0.069
6	"	0.02468	0.734	20.00		
7	"	0.01241	0.371	20.10		
8	"	0.00621	0.186	20.14		
9	glycerol	0.04496	0.935	13.99	14.01	0.022
10	"	0.03371	0.703	14.02		
11	"	0.01686	0.351	14.00		
12	"	0.00843	0.176	14.04		
13	1,2-propylene glycol	0.04032	0.667	11.13	11.13	0.100
14	"	0.03780	0.620	11.03		
15	"	0.03362	0.550	11.00		
16	"	0.02520	0.417	11.13		
17	"	0.01680	0.280	11.21	10.94	0.092
18	"	0.01260	0.211	11.26		
19	2,3-butylene glycol	0.09683	1.57	10.90		
20	"	0.07261	1.18	10.93		
21	"	0.03632	0.592	10.96	10.94	0.092
22	"	0.01816	0.294	10.89		
23	"	0.00908	0.150	11.11		
24	"	0.00454	0.073	10.81		
25	"	0.00227	0.037	10.96		

* Corrected for water impurity.

where c is the concentration of the reducing agent in milliequivalents per total volume of the mixed solution (sample solution plus oxidizing solution). This volume was constant throughout the experiments at an undetermined value in the vicinity of 50.00 ml. The factor, 10, in the denominator represents the length of the cell. Dextrose has 24 meq per mmol and sodium oxalate has 2 in accordance with the half-reactions.



These values of absorptivity are given in columns 5 and 6 of Table I.

The reduction capacities n of the polyols in milliequivalents per millimole were calculated by equation (4)

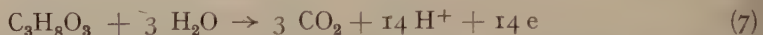
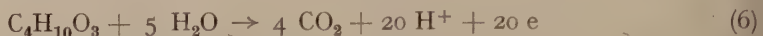
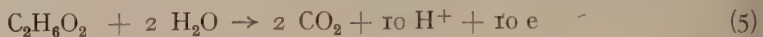
$$n = \frac{A}{10 \cdot ac'} \quad (4)$$

where c' is the concentration of the polyol in millimoles per total volume of the mixed solution. These values are given in columns 5 and 6 of Table II.

DISCUSSION

The constancy of the absorptivity values of Table I indicates that dextrose and sodium oxalate are quantitatively oxidized under the recommended conditions according to half-reactions (2) and (3), also that Beer's law is followed.

The complete oxidation of ethylene glycol, diethylene glycol, and glycerol to carbon dioxide may be represented by the half-reactions (5), (6), and (7), respectively.



The values of the calculated reduction capacities of these compounds in Table II check the values expected from the foregoing equations, indicating that quantitative oxidation of these polyols is obtained in the recommended procedure.

Propylene glycol may be oxidized according to half-reaction (8) or (9) with reduction capacities of 16 or 12, respectively.



The observed value of n in Table II is between these values, indicating a nonstoichiometric oxidation. However the empirical value of the reduction capacity, 11.13, is constant within the experimental error and may be used in the analysis of solutions of propylene glycol of unknown concentration. The fact that the reduction capacity found in the recommended procedure is higher than that found by CARDONE AND COMPTON³, 9.0, is probably due to the higher temperature developed on mixing the reagents in the recommended procedure.

Since the 2,3-butyleneglycol used in this investigation contained an unidentified impurity, the value of its reduction capacity in Table II, 10.94, cannot be interpreted with confidence. It is probable, however, that this glycol, because of its methyl groups, undergoes a nonstoichiometric oxidation like propylene glycol, which also contains a methyl group. The constancy of the observed n for the impure butyleneglycol probably means that both this glycol and its impurity have constant reduction capacities in the recommended procedure.

The absorptivity of 0.1487 found in these experiments does not represent the absorptivity of Cr(III) but is the difference between the absorptivity of Cr(III) and that of the dichromate (expressed also in milliequivalents per total volume) at the same wavelength, 610 m μ .

The absorbance of a blank prepared from a fresh oxidizing solution measured in a 10-cm cell against water is about 0.04. This is due in part to the absorbance of the dichromate and in part to Cr(III) formed by reducing impurities in the water or reagents. Blanks prepared from older oxidizing solutions have larger absorbances, probably because of a slow decomposition of the dichromate. However, the older oxidizing solutions may be used without sacrifice of accuracy because the error is eliminated by the use of a blank as the reference solution. For the same reason, it is not necessary to standardize the oxidizing solution.

SUMMARY

A rapid and accurate method is described for the determination of small quantities of polyhydroxy compounds by the spectrophotometric measurement of Cr(III) produced by the reduction of dichromate in 50% sulfuric acid. The method is probably applicable also to many other organic reducing agents. Duplicate determinations require only 30 minutes. The maximum standard deviation for any of the six compounds investigated was 0.90% of the polyol content.

RÉSUMÉ

Une méthode rapide et précise est décrite pour le dosage de petites quantités de composés polyhydroxylés, au moyen du dichromate en solution dans l'acide sulfurique à 50%; on dose le Cr(III) formé par spectrophotométrie. Cette méthode peut probablement s'appliquer également à beaucoup d'autres réducteurs organiques. Une double détermination peut s'effectuer en 30 minutes. L'erreur maximum pour chacun des six corps étudiés est de 0.90%.

ZUSAMMENFASSUNG

Man beschreibt eine Methode für die Bestimmung von kleinen Mengen von Polyoxyverbindungen durch die spektrophotometrische Messung des Cr(III), das bei der Reduktion des Dichromats in 50% iger Schwefelsäure entsteht. Die Methode ist wahrscheinlich auch für die Bestimmung von vielen anderen organischen Reduktionsmitteln anwendbar. Zweifache Bestimmungen dauern nur 30 Minuten. Der maximale Wert der Standardabweichung ist für jede der sechs untersuchten Verbindungen 0.90% des Gehaltes an Polyoxyverbindung.

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AMPEROMETRIC TITRATION OF MOLYBDENUM

by

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The need for a rapid and precise method for the determination of molybdenum in co-ordination compounds prompted the present investigation. The gravimetric lead molybdate method is too time consuming and a sample containing at least 10 mg of molybdenum is necessary to give the required accuracy. The lead titration procedure requires an external indicator and does not yield satisfactorily precise results.

This method of determining molybdates by precipitation with lead ions suggested the possibility of using lead nitrate solution as a reagent for the amperometric titration of molybdenum. THANHEISER AND WILLEMS¹ have determined molybdenum amperometrically by this method. The precipitation was carried out at 80° C from a potassium nitrate-sodium formate supporting electrolyte which also contained 15% ethanol. These authors used a mercury anode and worked at an applied e.m.f. of 0.6 V. At this voltage only the lead ions were reduced. The end-point was determined from the point where the current suddenly increased due to the addition of excess lead ions. KOLTHOFF AND LINGANE² have pointed out the disadvantages of not using the graphical method to determine this end-point. Furthermore, precipitating at this high temperature would require precise temperature control and special precautions to prevent loss of solvent by evaporation.

From the figures reported, the accuracy appears to be of the order of a few percent.

Several methods for the polarographic determination of molybdenum have been described. However, most of the supporting electrolytes used in these methods are not suitable solutions from which to precipitate lead molybdate. They either contain anions which form insoluble precipitates with lead ions^{3,4,5,6,7} or which form molybdenum complexes from which lead molybdate cannot be precipitated^{8,9,10}.

D. F. BOLTZ *et al.*⁶ used an acetic acid, acid sodium acetate buffer of pH = 3.5 to examine the polarographic reduction of molybdiphosphoric acid. Since this buffer closely resembles the conditions recommended for the quantitative precipitation of lead molybdate, the behaviour of molybdate ions in this supporting electrolyte was examined.

EXPERIMENTAL

Chemicals. Reagent grade ammonium molybdate was used. The molybdenum content was checked by the gravimetric lead molybdate method and found to contain 54.63 % Mo. All other chemicals used were of reagent grade purity.

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Apparatus. The current voltage curves in this research were obtained on a Tinsley chart recording polarograph. The reference electrode was a saturated calomel electrode which was connected to the electrolysis cell through a potassium chloride-agar bridge. The titrations were carried out in a jar using a manual polarograph of the type described by LINGANE AND KOLTHOFF¹¹. The galvanometer scale was divided into 100 divisions with full scale deflections of 2, 5, 10 and 20 μ A. The jar was fitted with a five-holed stopper to accommodate the dropping mercury electrode, the salt-bridge, the burette and two nitrogen inlets. The hole through which the dropping mercury electrode passed served as the nitrogen outlet. A burette of 5 ml capacity, graduated to 0.01 ml was used.

Polarographic behaviour of molybdenum(VI) in acetic acid buffer

Polarograms were run on $0.6 \cdot 10^{-3}$ M Mo solution in a supporting electrolyte 0.1M with respect to sodium acetate and potassium chloride and 1.0M with respect to acetic acid. Molybdenum (VI) is reduced at the dropping mercury electrode in this solution producing a double wave with half-wave potentials at about -0.24 and -0.54 V vs. S.C.E. Both waves are irreversible. The height of the second wave appears to be approximately twice that of the first wave (Figure 1). It was not possible to measure these waves accurately for no well-defined plateaux are formed.

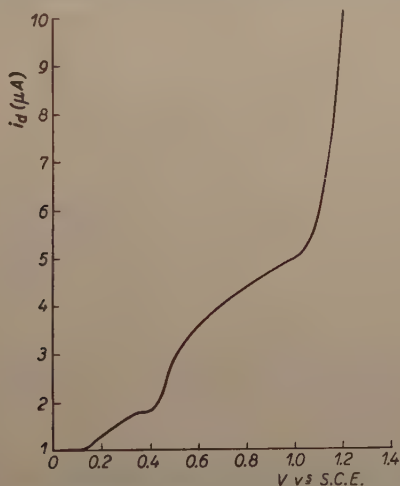


Fig. 1. Typical polarogram for reduction of Mo(VI) in supporting electrolyte 0.1M CH_3COONa ; 0.1M KCl ; 1.0M CH_3COOH

The investigation of these reduction curves was restricted to an examination of their application to amperometric titrations. The second step had a constant slope between -0.64 and -0.94 V vs. S.C.E. It appeared likely that this portion of the curve could be used to produce a diffusion current suitable for amperometric titration.

This was tested by carrying out a titration with lead nitrate and running a complete polarogram after each addition of titre. Excess lead ions produced a well defined reduction wave at -0.45 V vs. S.C.E. From the recorded polarograms, graphs were drawn for potentials of -0.6 , -0.7 , -0.8 , -0.9 and -1.0 V. The graphs (Fig.2) show that the equivalence points obtained at -0.7 , -0.8 , and -0.9 V coincide with one another and with the theoretical. The end-point at -0.6 V occurs before the equivalence point while the end-point at -1.0 V occurs after the equivalence point. On the basis of these results -0.8 V vs. S.C.E. was chosen as the control potential for the titration.

Procedure for amperometric titration of molybdenum

25 ml of the solution containing 0.3 to 3.0 mg of Mo as molybdate are pipetted into 25 ml of the supporting electrolyte of double strength contained in the titration vessel. Oxygen is removed from the solution by passing nitrogen for 10 minutes. A standard solution of lead nitrate (containing 4.25 g $\text{Pb}(\text{NO}_3)_2/\text{l}$) is then added in small increments. The volume of each addition depends on the total molybdenum content of the solution. Nitrogen is then bubbled through the solution for one minute. The pressure of the nitrogen is carefully adjusted at the beginning to cause a bubble to break over the tip of the burette to remove the last drop. The diffusion current is read at a potential of -0.8 V vs. S.C.E. one minute after diverting the gas over the

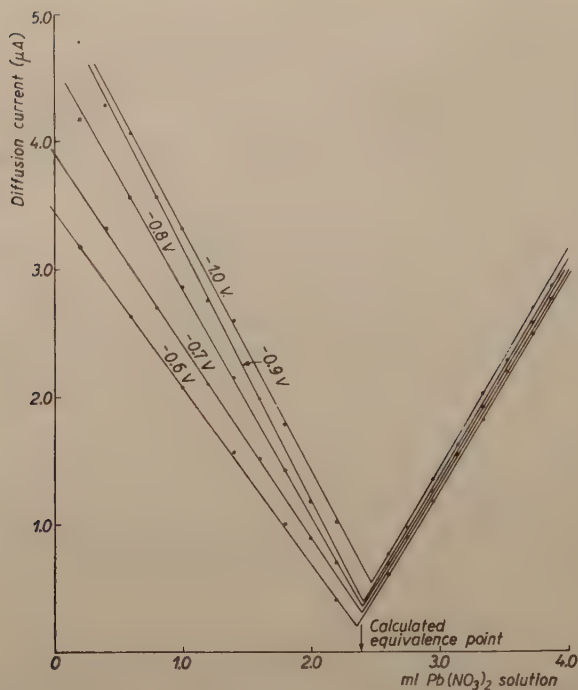


Fig. 2. Amperometric titration of Mo(VI) with $\text{Pb}(\text{NO}_3)_2$ solution at different control potentials

top of the solution. The readings thus obtained are plotted against ml of titre after correcting for the volume added. The equivalence point is obtained in the usual manner from the point where the two straight lines intersect.

Results

AMPEROMETRIC TITRATION OF MOLYBDENUM(VI) (mg MOLYBDENUM)

Taken	Found	Deviation	% error
2.980	2.998	+0.018	0.6
2.980	2.991	+0.011	0.4
2.980	3.003	+0.023	0.8
1.192	1.189	-0.003	0.25
1.192	1.193	+0.001	0.1
0.596	0.604	+0.008	1.3
0.596	0.599	+0.003	0.5
0.298	0.297	-0.001	0.3
0.298	0.297	-0.001	0.3
Average			0.4

The analytical precision, over the range tested, is about 0.4%. The lower limit of the method is 0.2 mg Mo in 50 ml of solution ($4 \cdot 10^{-5} M$). In more dilute solutions than this the addition of lead ions increases the diffusion current.

The method is readily applicable to the estimation of molybdenum in co-ordination compounds. The organic matter is destroyed with nitric acid and the solution evaporated to dryness. The residue is dissolved and the molybdate is titrated as described above. The estimation can be completed within thirty minutes. Phosphates, chromates, arsenates and sulphates interfere.

SUMMARY

A method for the amperometric titration of molybdenum(VI) with lead nitrate solution is described. The precipitation is carried out at room temperature from an acid sodium acetate-potassium chloride supporting electrolyte. The diffusion currents are recorded at a potential of -0.8 V vs. S.C.E. where both the lead and molybdenum give reduction waves. While the reduction of molybdenum in acetic acid buffer produces no well defined plateau, it gives accurate and reproducible results amperometrically. The analytical precision is about 0.4%.

RÉSUMÉ

Une méthode est décrite pour le dosage ampérométrique du molybdène(VI) au moyen d'une solution de nitrate de plomb. La précipitation est effectuée à la température ordinaire avec, comme électrolyte de base, une solution d'acétate de sodium — chlorure de potassium. Les courants de diffusion sont enregistrés au potentiel de -0.8 V (par rapport à l'électrode de calomel saturée) auquel soit le plomb, soit le molybdène donnent des vagues de réduction. La réduction du molybdène en tampon acétique ne donne pas de palier bien défini, tandis que les résultats obtenus par ampérométrie sont exacts et reproductibles. La précision analytique est d'environ 0.4 %.

ZUSAMMENFASSUNG

Es wird eine Methode zur amperometrischen Bestimmung von Molybdän(VI) mittels einer Bleinitratlösung beschrieben. Die Ausfällung wird bei gewöhnlicher Temperatur mit einer Lösung von Natriumazetat — Kaliumchlorid als Basiselektrolyt ausgeführt. Die Diffusionsströme werden beim Potential -0.8 V (in Bezug auf die gesättigte Kalomelelektrode) aufgenommen, bei welchem entweder das Blei oder das Molybdän Reduktionssprünge geben. Die Reduktion von Molybdän in einem Azetatpuffer gibt keinen gut definierten Sprung, während die durch Amperometrie erhaltenen Resultate exakt und reproduzierbare sind. Die analytische Präzision ist ungefähr 0.4%.

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HALF-WAVE POTENTIALS OF METAL IONS IN ORGANIC HYDROXYACID SUPPORTING ELECTROLYTES. I

by

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INTRODUCTION

Systematic information concerning the polarographic half-wave potentials of metal ions in various supporting electrolytes can be used in many ways. With its help, the practical analyst can often devise greatly simplified procedures for analysing complex solutions. It provides an immediate insight into the redox chemistry of the metal ions, and serves to indicate ways in which unfamiliar oxidation states can be prepared and stabilized. By identifying complexes which are reversibly reduced, it points the way to more detailed studies of the stoichiometry and thermodynamics of their formation.

Studies of this kind have been carried out recently by LINGANE⁵, by WEST, DEAN AND BREDA¹⁸, by PRIBIL and co-workers^{14,15,16}, by DESESA, HUME, GLAMM AND DEFORD², and by MEITES AND MEITES¹². The data presented in this paper were secured during the course of an investigation of the effect of the structure of an organic hydroxyacid on its ability to coordinate metal ions.

EXPERIMENTAL

The data in Table V were secured at the Louisiana State University with a photographically recording polarograph (E. H. Sargent and Co., Model XI) equipped with a d'Arsonval galvanometer. Some polarograms were obtained with a Heyrovsky-type cell, using a microcalomel reference electrode¹⁷ as the anode; others were obtained with a conventional H-cell⁶. The concentration of the metal ion was varied from 0.01 to 10 mM, and the malonate concentration from 0.25 to 0.50M, while the concentration of gelatin was kept constant at 0.01%.

The remaining data were secured at Yale University with a pen-and-ink recording polarograph¹⁰ whose initial and span e.m.f. voltmeters had been carefully calibrated with a Rubicon precision potentiometer. The measured half-wave potentials were corrected for the iR drops through both the polarograph and the modified H-cell¹¹ used. The operation of the apparatus was checked by frequently recording polarograms of cadmium(II) in 0.10M potassium nitrate. When the corrected value of $E_{1/2}$ differed by more than two or three millivolts from the literature value^{1,4,7}, the saturated calomel electrode and saturated potassium chloride agar bridge were replaced.

In these experiments the concentration of metal ion was always very nearly 1.0 mM, excepting that of thallous ion, which was always 0.2 mM. Unless otherwise noted in the Tables, no maximum suppressor was added.

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Reagent grade chemicals were used for the preparation of all solutions in both laboratories. The stock metal ion solutions employed at the Louisiana State University for the measurement of diffusion current constants were standardized by gravimetric or electrogravimetric methods. All solutions were deaerated with tank nitrogen or hydrogen, and Beckman Model G pH meters were used for all pH measurements. The drop times were always between 2.5 and 6 seconds.

The following symbols are used in the Tables. ">O" denotes a wave which begins at a potential so positive that it merges with the anodic wave due to dissolution of the electrode mercury, and carries no implication as to whether $E_{1/2}$ would actually be positive or negative if it could be measured. A value of $E_{1/2}$ enclosed in parentheses denotes an anodic wave. "NR" signifies that no wave is obtained. "w.-d." and "i.-d." mean well- and ill-defined, respectively, the criterion being the degree of accuracy with which, in our opinion, the height of the wave could be measured. A wave described as "very w.-d.", for example, is suited for the precise polarographic determination of the substance responsible for it; a "very i.-d." wave, on the other hand, merely serves to interfere with other waves, and is useless for any quantitative purpose whatever. Descriptions intermediate between these are necessarily matters of personal judgment.

The interpretation of these and other similar data derived from continuing work will be deferred until a later paper in this series.

TABLE I

HALF-WAVE POTENTIALS IN SATURATED CITRIC ACID

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Ag(I)	>0	o	Rounded max., very w.-d.
As(III)	-0.58	o(film?(3,9))	Very i.-d.
	-0.73	o	I.-d.
	-1.02	-III	I.-d., max. not suppressed by 0.002% Triton X-100
As(V)	NR		
Bi(III)	-0.025	o	W.-d., slightly irreversible
Cd(II)	-0.514	o	Very w.-d., reversible
Ce(III)	NR		
Ce(IV)	-		Rapidly reduced to Ce(III), <i>q.v.</i>
Co(II)	NR		
Cr(III)	-0.78	II	I.-d., reversible
Cr(VI)	>0	III	Large rounded max., w.-d., no indication of wave at -0.78 V
Cu(II)	+0.03	o	Small max., very w.-d., slightly irreversible
Fe(II)	NR		
Fe(III)	+0.23	II	W.-d., reversible
In(III)	-0.540	o	W.-d., irreversible
Mn(II)	NR		
Mo(VI)	+0.038	V	Very w.-d., reversible
	-0.437	III	Very w.-d., irreversible
Ni(II)	-0.98	o	I.-d., irreversible
Pb(II)	-0.358	o	W.-d., reversible
Sb(III)	-0.376	o	Very w.-d., irreversible
Sb(V)	NR		
Sn(II)	(-0.05)	IV	Fairly w.-d., reversible
	-0.40	o	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	-0.442	o	Very w.-d., reversible
U(VI)	-0.122	IV(?)	Very w.-d.; $E_{1/2}-E_{1/4} = -63$ mV
V(IV)	-0.67	?	Small i.-d. pre-wave
	-1.05	II	I.-d., irreversible
V(V)	+0.108	IV	Very w.-d., reversible
	-0.63	II	Fairly i.-d., irreversible
W(VI)	NR		
Zn(II)	-0.930	o	Fairly i.-d., reversible

TABLE II
 HALF-WAVE POTENTIALS IN SATURATED MALONIC ACID

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(III)	-0.70	o(?)	Fairly i.-d., irreversible; may actually be poorly resolved double wave
As(V)	NR		
Bi(III)	+0.010	o	Large max. nearly unaffected by 0.002% Triton X-100, very w.-d.
Cd(II)	-0.519	o	Reversible, very w.-d.
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), <i>q.v.</i>
Co(II)	NR		
Cr(III)	-0.8 ₅	II(?)	Very small, very i.-d.
Cr(VI)	>0	III	Huge max., very w.-d.; height is only about 2/3 the predicted value for $n = 3$
Cu(II)	+0.081	o	Very w.-d., slightly irreversible
Fe(II)	NR		
Fe(III)	>0	II	Very w.-d.
Fe(III) ^a	+0.202	II	Very w.-d., reversible
In(III)	-0.504		Very i.-d.
	-0.61	o	Plateau has abnormally large positive slope. Waves are due to two species in sluggish equilibrium.
Mn(II)	NR		
Mo(VI)	+0.073	V	Very w.-d., irreversible
	-0.228	III	Very w.-d., slightly irreversible
Ni(II)	-0.97	o	I.-d., irreversible
Pb(II)	NR		Complete pptn.; $E_{1/2} = -0.375$ V for very w.-d. reversible wave in half-saturated malonic acid
Sb(III)	-0.118	o	Very w.-d., nearly reversible
Sb(V)	NR		
Sn(II)	(+0.015)	IV	Fairly w.-d., nearly reversible
	-0.397	o	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR(?)		Final current rise starts abnormally early, at -0.95 V
Tl(I)	-0.440	o	Reversible
U(VI)	-0.12	IV	Very w.-d.; $E_{1/2} - E_{1/4} = -57$ mV
	-1.1(?)		Some indication of an i.-d. irreversible wave
V(IV)	-0.64		Pre-wave
	-1.08	II	Very i.-d., very irreversible
V(V)	>0	IV	Fairly w.-d.
	-0.67	II(?)	
W(VI)	NR(?)		Final current rise starts at -0.8 V, but no plateau is found: catalytic reduction of H ⁺ ?
Zn(II)	-0.9 ₄	o	Very i.-d.

a: with 0.002% Triton X-100

 TABLE III
 HALF-WAVE POTENTIALS IN SATURATED TARTARIC ACID

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Ag(I)	>0	o	Small rounded max., w.-d.
As(III)	-0.37		Fairly w.-d.
	-0.45		Rounded max., i.-d.
	-0.62	-III	Fairly w.-d.

TABLE III (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(V)	-1.0		Very i.-d.
Bi(III)	-0.06 ₀	o	W.-d., slightly irreversible
Cd(II)	-0.564	o	Very w.-d., reversible
Ce(IV)	+0.25	III	
Co(II)	NR		
Cr(III)	-0.91	II	Very i.-d., irreversible
Cr(VI)	-		Rapidly reduced to Cr(III), <i>q.v.</i>
Cu(II)	>0		I.-d.
	-0.08		I.-d.
	-0.34		Very w.-d.
Fe(II)	NR		
Fe(III)	>0	II	W.-d.
In(III)	-0.527	o	Reversible; plateau has abnormally large positive slope
Mn(II)	NR		
Mo(VI)	-0.08 ₄	V	Fairly w.-d., irreversible
	-0.391	III	Very w.-d., irreversible
Ni(II)	-1.05	o	Fairly i.-d.
Pb(II)	-0.40	o	Very w.-d., reversible
Sb(III)	-0.41	o	Very w.-d., slightly irreversible
Sb(V)	NR		
Sn(II)	(-0.08)	IV	W.-d., reversible
	-0.44	o	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	-0.83	?	Abnormally small
Tl(I)	-0.473	o	Very w.-d., reversible
U(VI)	-0.11 ₅	IV(?)	W.-d., rounded max.; $E_{1/4}^{\text{U}} - E_{1/4}^{\text{U}} = -51$ mV
V(IV)	+0.03	II	} Two small i.-d. irreversible waves
	-0.40		
	-0.75		
V(V)	+0.25	IV	Fairly w.-d.
	-0.75	II	I.-d., very irreversible
W(VI)	-0.9		Some indication of a very irreversible wave; <i>cf.</i> Table II
Zn(II)	-1.03	o	Fairly w.-d.

TABLE IV

HALF-WAVE POTENTIALS IN 0.5*M* SODIUM HYDROGEN MALONATE — 0.5*M* DISODIUM MALONATE, pH 4.8

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(III)	-1.00	?	Very i.-d.
As(V)	NR		
Bi(III)	-0.195	o	Very w.-d., slightly irreversible
	-1.20		Anomalous ^{a,13}
Cd(II)	-0.648	o	Very w.-d., reversible
	-1.17		Anomalous ^a
Ce(IV)	>0	III	Very w.-d.
	-1.16		Anomalous ^a
Co(II)	NR		
Cr(III)	-1.0	II	Small, i.-d., very irreversible ^a
Cr(VI)	>0	III	Large max., very w.-d.
	-1.16		Anomalous ^a
Cu(II)	-0.170	o	Very w.-d., reversible
	-1.16		Anomalous ^a

TABLE IV (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Fe(II)	(-0.250)	III	Very w.-d., reversible
Fe(III)	-0.255	II	Very w.-d., reversible
	-1.16		Anomalous ^a
Fe(III) ^b	-0.250	II	Very w.-d., reversible
In(III)	-0.19	?	} Both very i.-d. and almost completely eliminated by 0.004% Triton X-100
	-0.72	?	
Mn(II)	NR		
Mo(VI)	-0.67	IV	Fairly i.-d., very irreversible
	-1.21	III	Fairly i.-d., irreversible
Ni(II)	-1.13	}	I.-d. triple wave ^a
	-1.28		
	-1.50		
Pb(II)	-0.48 ₁	o	Very w.-d., reversible
	-1.16		Anomalous ^a
Sb(III)	-0.47 ₈	o	Small acute max. on rising portion of wave simulates double wave; very w.-d., slightly irreversible
Sb(V)	NR		
Sn(II)	(-0.293)	IV	Very w.-d., reversible
	-0.605	o	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	-1.17		Fairly i.-d., irreversible
Tl(I)	-0.474	o	Very w.-d., reversible
	-1.16		Anomalous ^a
U(VI)	-0.437	IV	Very w.-d.; $E_{3/4} - E_{1/4} = -51$ mV
	-1.19	III	Very i.-d., very irreversible
V(IV)	-1.34	II	Very i.-d., irreversible
V(V)	>0	IV	Very w.-d.
	-1.33	II	I.-d., irreversible
W(VI)	-1.38	?	Large acute max., i.-d.
W(VI) ^b	-1.39	III(?)	Fairly w.-d.; $E_{3/4} - E_{1/4} = -46$ mV
Zn(II)	-1.14 ₆	o	Fairly w.-d., reversible

a: Eliminated by 0.002% Triton X-100

b: With 0.002% Triton X-100

TABLE V

HALF-WAVE POTENTIALS IN 0.5*M* MALONATE - 0.01% GELATIN, pH 0.1-9

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Ag(I)	>0.	o	Rapidly reduced by Hg pool
Al(III)	NR		
Au(III)			
(AuCl ₄) ⁻	NR		
Bi(III)	-0.084	o	pH 2.18, w.-d., irreversible. $I = 3.72$. Unsatisfactory at pH < 2
Bi(III)	-0.196	o	pH 4.54, w.-d., irreversible. $I = 3.72$
Bi(III)	-0.248	o	pH 5.69, w.-d., irreversible. $I = 3.72$
Cd(II)	-0.65 ₇ ± 0.01 ₂	o	pH 4.6-6, w.-d., reversible. $I = 2.93$. Unsatisfactory at pH < 4.5
Co(II)	NR		
Cr(III)	NR		
Cu(II)	-0.006 ± 0.002	o	pH 0.1-1.5, very w.-d., reversible. $I = 3.55$. Unsatisfactory with < 0.1 mM Cu(II)

TABLE V (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
I(V) (IO_3^-)	-0.77	-I	pH < 4.0, w.-d., irreversible. $I = 9.94$
I(V) (IO_3^-)	-0.77		4.0 ≤ pH ≤ 6.0. $I_{\text{total}} = 9.94$
I(V) (IO_3^-)	-1.14	-I	
I(V) (IO_3^-)	-1.14	-I	pH > 6.0. $I = 9.94$
Ir(IV)	NR		
Mn(II)	NR		
Ni(II)	NR		
Os(VIII)	NR		
Pb(II)	-0.495 ± 0.002	o	pH 5.7-6.0, 1 mM Pb(II), w.-d., reversible. $I = 3.29$
Pt(IV)	NR		
Sb(III)	not satisfactorily measurable		Poorly resolved double wave (second wave begins at ca. -0.3 V)
Se(IV)	-0.742	o(?)	pH 5.2-5.8, 1 mM Se(IV), fairly w.-d., irreversible. $I = 5.06$
Se(IV)	-0.802	o(?)	pH 5.2-5.8, 5 mM Se(IV), fairly w.-d., irreversible
Se(IV)	-0.74	o(?)	pH > 5.8
Se(IV)	-1.41	?	$E_{1/2}$ independent of Se concn.
Se(VI)			Virtually identical with Se(IV) in every respect
Sn(II)	(-0.265)	IV	
Sn(II)	-0.664	o	
Sn(IV)	NR		
Te(VI)	-1.57	o(?)	pH 5.7-8.7, 0.06 mM Te(VI), w.-d., irreversible, $\Delta E_{1/2} / \Delta \log [\text{Te(VI)}] = -0.060$ V
Te(VI)	-1.33	o(?)	pH 5.64, 0.06 mM Te(VI), w.-d., irreversible, $\Delta E_{1/2} / \Delta \log [\text{Te(VI)}] = -0.060$ V
Te(VI)	-1.30	o(?)	pH 4.95, 0.06 mM Te(VI), w.-d., irreversible, $\Delta E_{1/2} / \Delta \log [\text{Te(VI)}] = -0.060$ V
Te(VI)	-		pH 4.07, 0.06 mM Te(VI), very i.-d.
Tl(I)	-0.492 ± 0.006	o	pH 2.2-5.6, 0.01 mM Tl(I), very w.-d., reversible. $I = 2.46$

TABLE VI

HALF-WAVE POTENTIALS IN 1M DISODIUM MALONATE — 0.2M SODIUM CARBONATE — 0.2M SODIUM BICARBONATE, pH 10.0

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(III)	(-0.02)	V	Very i.-d., slightly irreversible
As(V)	NR		
Bi(III) ^a	-0.51 ₉	o	Very w.-d., slightly irreversible
Bi(III) ^a	-1.29		Anomalous ^b
Cd(II) ^a	-0.692	o	Very w.-d., reversible
Cd(II) ^a	-1.28		Anomalous ^b
Ce(IV)	-0.058	III	W.-d., reversible
Ce(IV)	-1.25		Anomalous ^c
Co(II)	-1.59	o	Fairly w.-d., very irreversible
Cr(III)	NR		
Cr(VI)	-0.40	III	I.-d.; shape greatly improved by 0.002% ₀ Triton X-100
Cu(II)	-0.220	o	Very w.-d., reversible
Cu(II)	-1.31		Anomalous ^b

TABLE VI (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Fe(II)	(-0.512)	III	Very w.-d., reversible
	-1.62	o	Fairly w.-d., irreversible
Fe(III)	-0.518	II	W.-d., reversible
	-1.65	o	I.-d., irreversible
In(III)	-1.32	o	Very w.-d., irreversible, probably includes anomalous wave
In(III) ^d	-1.30	o(?)	Very i.-d., very irreversible
	-1.61		Probably anomalous
Mn(II)	NR		
Mo(VI)	NR		
Ni(II)	-1.14		Very i.-d., irreversible
	-1.36		Fairly i.-d., irreversible
Pb(II) ^a	-0.616	o	Very w.-d., reversible
	-1.28		Anomalous ^c
Sb(III)	(-0.12 ₂)	V	W.-d., irreversible
	-0.864	o	W.-d., nearly reversible
Sb(V)	-0.1 ₄		} Four very small, fairly w.-d., irreversible waves
	-0.4 ₆		
	-0.8 ₈		
	-1.2 ₆		
Sn(II)	(-0.638)	IV	Very w.-d., irreversible
	-0.817	o	Very w.-d., reversible
	-1.28		Anomalous
Sn(IV)	-1.25	o(?)	I.-d., very irreversible
Sn(IV) ^d	-1.22	II(?)	Very i.-d., irreversible
	-1.64	o(?)	Probably not anomalous; total wave height is unaffected by Triton
Te(VI)	-1.38	?	Fairly i.-d.
Tl(I)	-0.483	o	Very w.-d., reversible
	-1.30		Anomalous ^b
U(VI)	-0.90	V	Fairly i.-d., irreversible
	-1.29		Anomalous ^b
V(IV)	(-0.380)	V	Very w.-d., slightly irreversible
	-1.17		Very irreversible pre-wave
	-1.59	II	Fairly i.-d., irreversible
V(V)	-1.18	IV	Very i.-d., irreversible
	-1.59	II	Fairly w.-d., irreversible
W(VI)	NR		
Zn(II)	-1.28 ₅	o	W.-d., irreversible

a: Extensive precipitation from a 1 mM solution

b: Shifted to -1.62 ± 0.02 V and considerably decreased in height by 0.002% Triton X-100

c: Eliminated by 0.002% Triton X-100

d: With 0.002% Triton X-100

TABLE VII

HALF-WAVE POTENTIALS IN 1M DISODIUM MALONATE — 1M SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(III)	(-0.273)	V	W.-d., reversible
As(V)	-1.1 ₄		Very small, i.-d.
Bi(III)	-0.68 ₆	o	W.-d., slightly irreversible
	-1.23		Anomalous
Cd(II) ^a	-0.94		Decreases on standing
	-1.20		Probably anomalous
	-1.55		Increases on standing

} all i.-d.

TABLE VII (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Cd(II) ^{a,b}	-0.86 -1.59		Very small, i.-d., irreversible I.-d., probably anomalous
Ce(III) ^a	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), <i>q.v.</i>
Co(II)	-1.52	o	Small, very i.-d., irreversible
Cr(III)	-0.92	II	Small, w.-d., reversible
Cr(VI)	-0.75 -1.16	III	Fairly w.-d., irreversible Probably anomalous
Cr(VI) ^b	-0.77 ₀	III	W.-d., irreversible
Cu(II)	-0.35 ₇ -0.44 ₇ -1.26	o	Very i.-d. } both reversible; two complexes Very w.-d. } in sluggish equilibrium Anomalous
Cu(II) ^b	-0.36 ₆ -0.44 ₈ -1.55	o	I.-d. } <i>vide supra</i> Very w.-d. } Anomalous
Fe(II) ^a	(-0.96)	III	
	-1.56	o	Very small; fairly w.-d.
Fe(III)	-0.90 -1.19	II	Fairly i.-d., irreversible Anomalous
	-1.57	o	Fairly i.-d., slightly irreversible
Fe(III) ^b	-0.89 -1.61	II	Fairly w.-d., irreversible I.-d., irreversible, includes anomalous wave
In(III)	-1.12	o(?)	W.-d., irreversible, includes anomalous wave
Mn(II) ^a	(-0.43) -1.72 -0.90	III(?) o ?	Very small, i.-d., irreversible Very i.-d., slightly irreversible Very small, irreversible
Mo(VI)	NR		
Ni(II)	NR		
Pb(II)	-0.754 -1.29	o	Very w.-d., reversible Anomalous
Pb(II) ^b	-0.757	o	Very w.-d., reversible
Sb(III)	(-0.47 ₅) -1.13 ₇ -1.41	V o	Very w.-d., slightly irreversible Fairly i.-d., irreversible Possibly anomalous
Sb(V)	NR		
Sn(II)	(-0.95 ₂) -1.13 ₇ -1.39	IV o	Large acute max., very w.-d. Large acute max., i.-d. Anomalous
Sn(II) ^b	(-0.934) -1.14 ₈ -1.60	IV o	Very w.-d., slightly irreversible W.-d., slightly irreversible Anomalous
Sn(IV)	NR		
Te(VI)	-1.52		Fairly i.-d., irreversible
Tl(I)	-0.477 -1.29	o	Very w.-d., reversible Anomalous
U(VI)	-0.908 -1.24 -1.63	V(?)	Fairly w.-d., reversible (?) } Two i.-d. very irreversible waves of approxi- } mately equal heights
U(VI) ^b	-0.906 -1.60	V(?) IV(?)	Very w.-d., reversible (?) I.-d., very irreversible
V(IV)	(-0.44 ₀) -1.68	V II	Very w.-d., irreversible Very i.-d., irreversible
V(V)	-1.67 ₄	II	Very i.-d., irreversible
W(VI)	-0.90 -1.22	?	Small, fairly w.-d. Probably anomalous
W(VI) ^b	-0.90	?	Small, w.-d.
Zn(II)	-1.482	o	Very w.-d., irreversible

a: Extensive precipitation from a 1 mM solution

b: With 0.002% Triton X-100

TABLE VIII

HALF-WAVE POTENTIALS IN 1M SODIUM LACTATE — 1M SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Ag(I) ^a	>0	o	
As(III)	(-0.27)	V	Fairly w.-d., nearly reversible
As(V)	NR		
Bi(III)	-0.71 ₅ -1.10	o	Fairly i.-d., slightly irreversible Anomalous
Cd(II)	-0.83 -1.12	o	Small, fairly w.-d. Anomalous
Ce(III)	NR		
Ce(IV)	-		Rapidly reduced to Ce(III), <i>q.v.</i>
Co(II)	-1.62	o	Very i.-d., irreversible
Cr(III)	NR		
Cr(VI)	-0.80	III	Very w.-d.
Cu(II)	-0.51 ₅ -1.13	o	W.-d., slightly irreversible Anomalous
Fe(II)	(-0.98) -1.66	III o	W.-d., reversible Fairly w.-d., slightly irreversible
Fe(III)	-1.00 -1.67	II o	Irreversible Slightly irreversible
Mn(II)	(-0.46) -1.76	III(?) o	Abnormally small, irreversible Fairly w.-d., nearly reversible
Mo(VI)	NR		
Ni(II) ^a	NR		
Pb(II)	-0.772 -1.11	o	I.-d., reversible Anomalous
Pb(II) ^b	-0.771 -1.41	o	Very w.-d., reversible Anomalous
Sb(III)	(-0.46) -1.17	V o	Very w.-d., slightly irreversible W.-d., irreversible
Sb(V)	NR		
Sn(II)	(-0.95) -1.15	IV o	Very w.-d., nearly reversible Very w.-d., nearly reversible, includes anomalous wave ($i_c > i_a$)
Sn(IV)	>0 -1.09 -1.48		} Three small waves of approximately equal heights. No waves observed with 5 mM Sn(IV)
Sn(IV) ^b	>0 -1.6		
Te(VI)	-1.54	o(?)	Fairly w.-d., irreversible
Tl(I)	-0.485 -1.09 -1.34	o	Fairly w.-d., reversible } Two very irreversible waves
Tl(I) ^b	-0.485 -1.40 -1.66	o	Very w.-d., reversible } Fairly w.-d., irreversible
U(VI)	-0.95 -1.7	V(?) IV(?)	I.-d. Very i.-d.
U(VI) ^b	-0.93 -1.67	V IV(?)	Fairly w.-d., reversible Fairly i.-d., irreversible
V(IV)	(-0.51) -1.70	V II	W.-d., reversible Very i.-d., irreversible
V(V)	-1.71	II(?)	Very i.-d., very irreversible
W(VI)	-1.1	?	Abnormally small, irreversible, eliminated by 0.002% Triton X-100
Zn(II)	-1.50	o	W.-d., slightly irreversible

^a: Extensive precipitation from a 1 mM solution^b: With 0.002% Triton X-100

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SUMMARY

Eight new media containing organic hydroxyacids and their anions have been investigated as supporting electrolytes for polarographic analysis. For over 25 metal ions in each of these media there are tabulated the half-wave potentials, reversibilities and probable products of the electrode reactions, descriptions of the wave forms, and other data of polarographic importance.

RÉSUMÉ

Huit nouveaux milieux, renfermant des hydroxyacides et leurs sels, ont été étudiés comme électrolytes de base dans l'analyse polarographique, pour plus de 25 cations. Les potentiels de demi-onde, les réversibilités et les produits de réaction aux électrodes, les descriptions des formes des ondes et d'autres renseignements polarographiques sont donnés dans des tableaux.

ZUSAMMENFASSUNG

Es wurden acht neue Medien, welche Hydroxysäuren und ihre Salze enthalten, als Basiselektrolyte in polarographischen Analysen für mehr als 25 Kationen untersucht. Die Halbwertspotentiale, die Reversibilität und die Reaktionsprodukte an den Elektroden, die Beschreibung der Form der Wellen und andere polarographische Einzelheiten werden in Tabellen angegeben.

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BUCHBESPRECHUNG

Leichtmetallanalyse, von H. GINSBERG, 3. Auflage, Verlag Walter de Gruyter u. Co., Berlin 1955, XIX + 285 Seiten, 79 Abb., Ganzleinen 24,80 DM.

Die nunmehr vorliegende 3. Auflage dieses Buches unterscheidet sich wesentlich von den früheren Auflagen. Gliederung und Anordnung des Stoffes ist vollständig umgestaltet und auch der Inhalt ist in Vielem abgeändert worden, um den Fortschritten der analytischen Arbeitsmethodik seit der letzten Auflage Rechnung zu tragen.

In einem allgemeinen Teil wird zunächst die Probenahme und die Vorbereitung der Proben für die chemische Analyse getrennt für Aluminium verschiedenen Reinheitsgrades, Beryllium, Magnesium und Titan, sowie die Probenahme und Vorbereitung der Proben für die Spektralanalyse besprochen. Der Referent würde es allerdings begrüßen, wenn wegen der grundlegenden Bedeutung der Probenahme für jede analytische Untersuchung, die Ausführungen zu diesem Punkte etwas umfangreicher wären und mehr in's Einzelne gingen. Ferner wird eine Zusammenstellung der verschiedenen Möglichkeiten zum Auflösen von metallischem Aluminium, Beryllium, Magnesium und Titan gegeben und schließlich werden in einem „Meßmethoden und Meßgeräte“ überschriebenen Kapitel einige allgemein gehaltene Bemerkungen über Gewichtsanalyse, Maßanalyse, elektrolytische Verfahren, Polarographie, Kolorimetrie und Photometrie, Flammenphotometrie und Spektrographie gemacht.

In den dann folgenden speziellen Teilen wird die Analyse der Metalle Aluminium (153 Seiten), Beryllium (12 Seiten), Magnesium (25 Seiten), Titan (32 Seiten) und ihrer Legierungen behandelt. Auch einige orientierende Kurzmethode, die dazu dienen können, die Legierungsgattung zu bestimmen, zu der das Material eines beliebigen Werkstückes zu zählen ist, sind angegeben. Im Interesse der Schnelligkeit bei der Analysendurchführung zieht man es heute im Allgemeinen vor, die einzelnen Elemente unter Verwendung gesonderter Einwagen und spezieller Verfahren in Einzelbestimmungen zu ermitteln. Der Verfasser hat deshalb die in den früheren Auflagen gebrachten Trennungsgänge fortfallen lassen und gibt dafür Arbeitsvorschriften zur Bestimmung jeweils nur eines Bestandteiles für ein bestimmtes vorliegendes Probematerial. Diese Arbeitsvorschriften sind aber so gestaltet, daß es für den Erfahrenen leicht ist, sich im Bedarfsfalle einen geeigneten Trennungsgang zusammenzustellen.

Die in früheren Auflagen benutzte Anordnung des Stoffes nach den Arbeitsweisen ist zugunsten einer alphabetischen Ordnung nach den zu bestimmenden Elementen aufgegeben worden. Es muß dies als eine wesentliche Verbesserung bezüglich der Übersichtlichkeit und der Bequemlichkeit bei der praktischen Verwendung des Buches bezeichnet werden.

Bei der Besprechung der zur Bestimmung der einzelnen Bestandteile vorgeschlagenen Verfahren werden zunächst deren Grundlagen, Anwendungsbereich, Genauigkeit und Störungen kurz beschrieben und besondere Hinweise für ihre Durchführung gegeben; es folgt dann eine Zusammenstellung der erforderlichen Reagenzien und eine Arbeitsvorschrift. Hervorzuheben ist die übersichtliche Darstellung des Gebotenen, die in straffer Zusammenfassung nur das Wesentliche, aber dieses mit einer für den erstrebten Zweck völlig genügenden Ausführlichkeit bringt. Häufig werden zur Bestimmung eines Elementes mehrere verschiedene Wege angegeben. Bei photometrischen Verfahren sind durchweg die Extinktionskurven der zu messenden gefärbten Lösungen abgebildet.

Von einer Bevorzugung einer bestimmten Gruppe von Verfahren bei den zur Bestimmung der verschiedenen Elemente gegebenen Arbeitsvorschriften kann keine Rede sein. So finden sich neben Methoden, die seit Jahrzehnten bekannt und bewährt sind Verfahren, die erst in allerletzter Zeit entwickelt wurden; neben rein chemischen werden auch physikalische Verfahren vorgeschlagen. Daß die polarographischen und besonders die photometrischen Verfahren gegenüber den früheren Auflagen hier einen breiteren Raum einnehmen, ist eine Folge der immer weiter gesteigerten Reinheit technisch dargestellter Metalle, wodurch auch im Rahmen von Routine-Analysen die Durchführung von Spurenbestimmungen erforderlich wird. Dies ist bei der Auswahl der beschriebenen Analysenverfahren berücksichtigt worden.

Es liegt in der Natur eines Buches, das von einem Praktiker für die Praxis geschrieben wurde, daß eine Vollständigkeit bei der Darstellung der verschiedenen Möglichkeiten nicht angestrebt wird, sondern daß aus der Fülle der bekannten Verfahren diejenigen herausgestellt werden, die zuverlässig, schnell, wenig störanfällig und einfach durchzuführen sind und die sich im Laufe einer längeren Laboratoriumspraxis als für einen bestimmten Fall besonders geeignet erwiesen haben. Diese Auswahl ist dem Verfasser vorzüglich gelungen. Man darf deshalb die vorliegende 3. Auflage der „Leichtmetallanalyse“ wohl als eine Standardsammlung der bei der Untersuchung entsprechender Materialien anzuwendenden Analysenverfahren bezeichnen. Sie dürfte z.Z. auf keine normalerweise bei der Analyse von Leichtmetallen gestellte Frage die Antwort schuldig bleiben und wird deshalb jedem, der auf diesem Gebiet zu arbeiten hat, schon nach kurzem Gebrauche unentbehrlich werden.

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